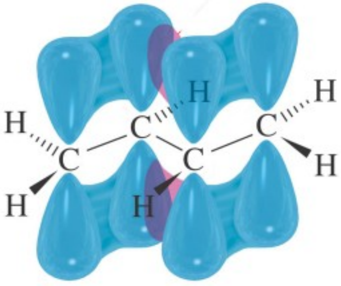
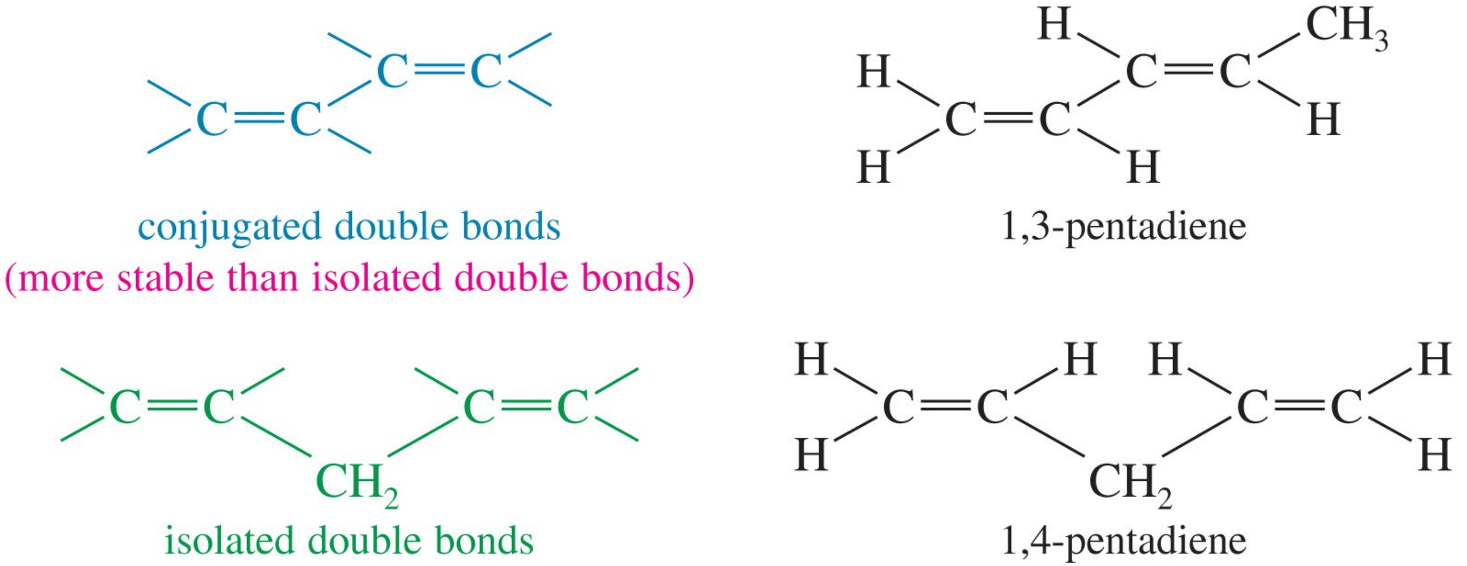
Organic Chemistry, 7th Edition
L. G. Wade, Jr.



Chapter 15

Conjugated Systems, Orbital Symmetry, and Ultraviolet Spectroscopy

Conjugated Systems


conjugated double bonds

(more stable than isolated double bonds)

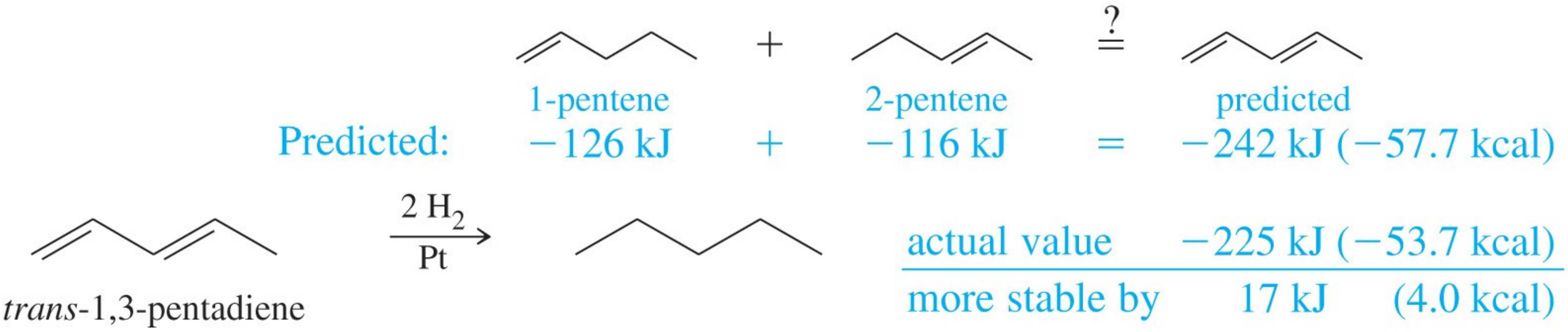
1,3-pentadiene

isolated double bonds

1,4-pentadiene

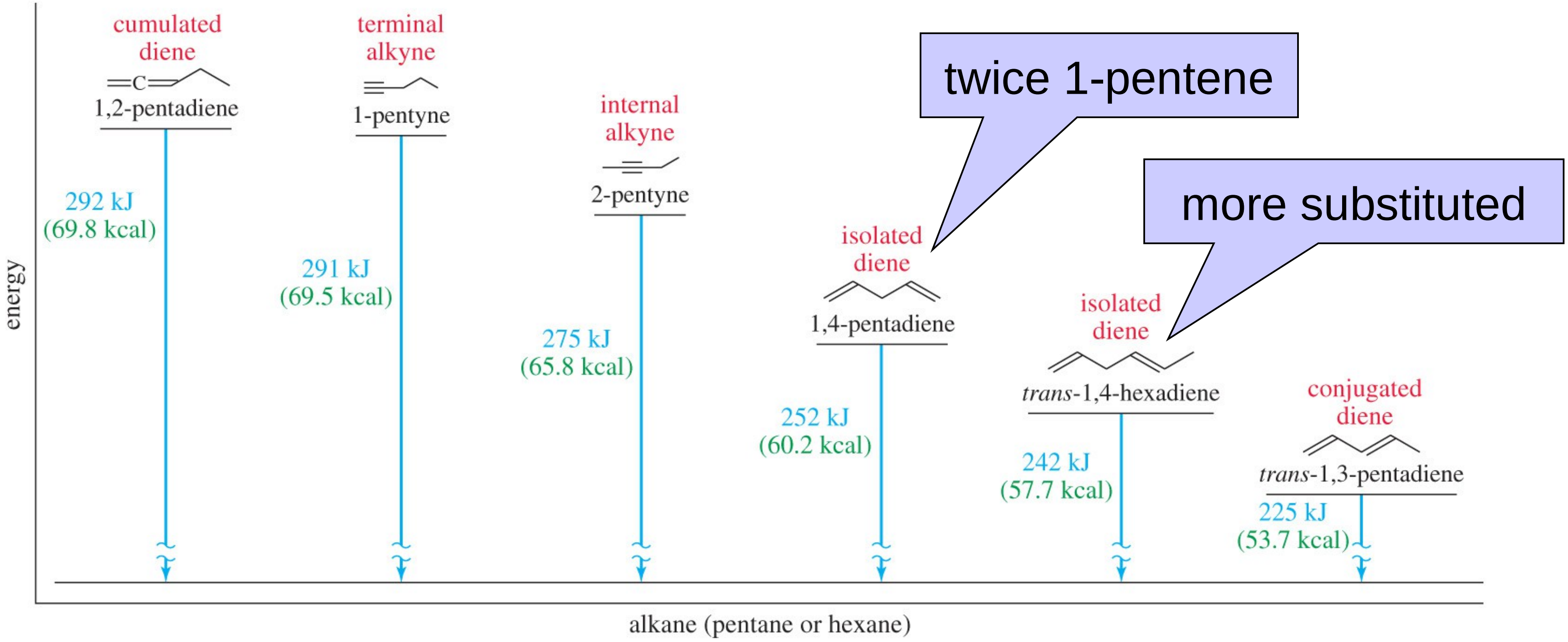
- Conjugated double bonds are separated by one single bond.
- Isolated double bonds are separated by two or more single bonds.
- Conjugated double bonds are more stable than isolated ones.

Heat of Hydrogenation of Conjugated Bonds



- For conjugated double bonds, the heat of hydrogenation is less than the sum for the individual double bonds.
- The more stable the compound, the less heat released during hydrogenation,
- Conjugated double bonds have extra stability.

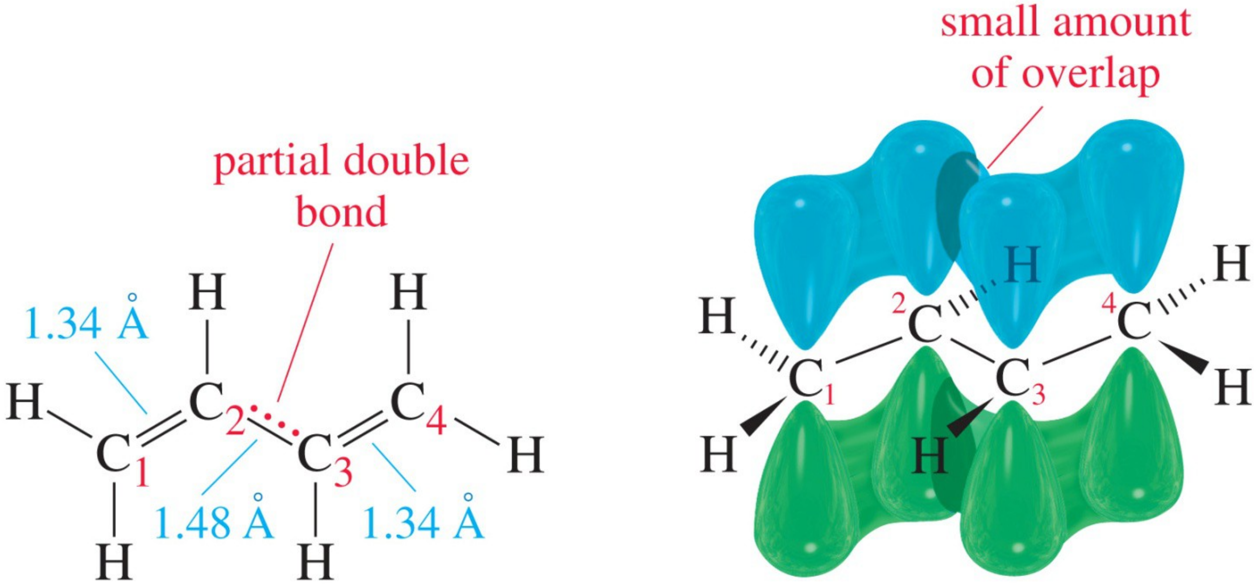
Relative Stabilities



twice 1-pentene

more substituted

Structure of 1,3-Butadiene

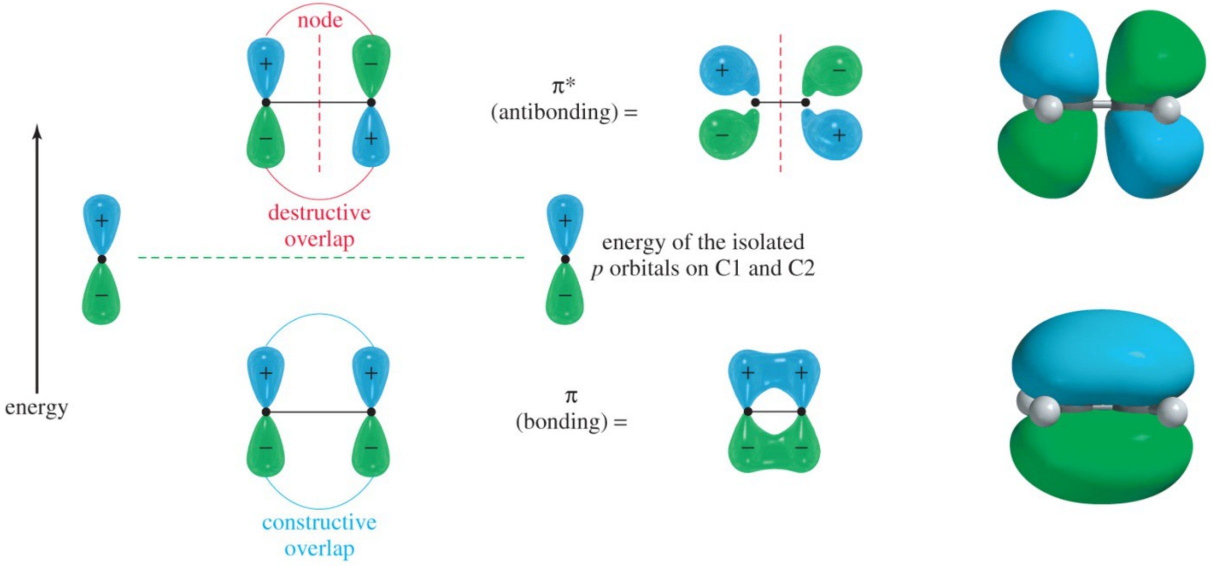


- Single bond is shorter than 1.54 Å.
- Electrons are delocalized over molecule.
- There is a small amount of overlap across the central C—C bond, giving it a partial double bond character.

Molecular Orbitals (MOs)

- Pi molecular orbitals are the sideways overlap of *p* orbitals.
- *p* orbitals have two lobes. Plus (+) and minus (-) indicate the opposite phases of the wave function, <u>not</u> electrical charges.
- When lobes overlap constructively (+ and +, or - and -), a bonding MO is formed.
- When + and - lobes overlap, waves cancel out and a node forms; antibonding MO.

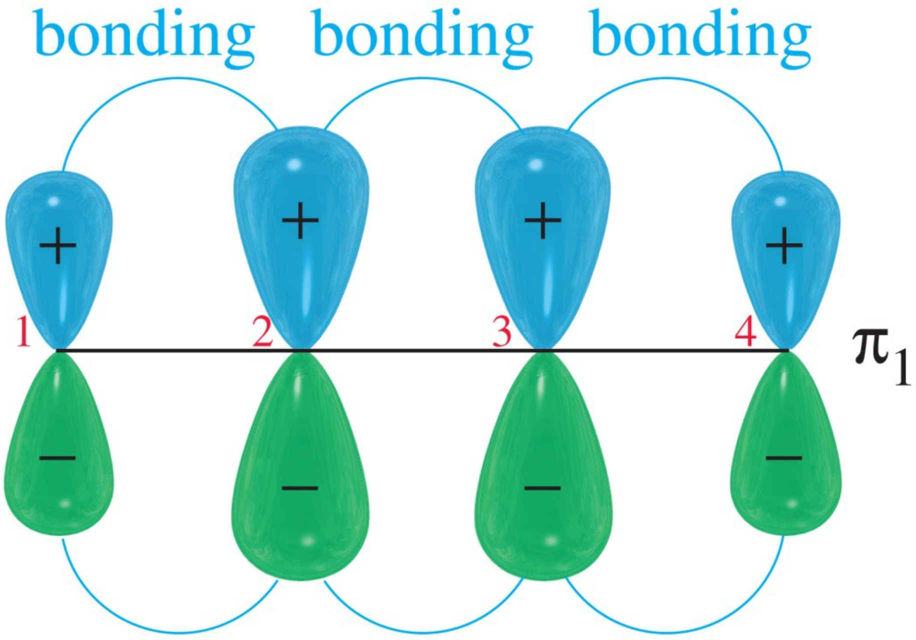
Ethylene Pi MOs



- The combination of two *p* orbitals must give two molecular orbitals.
- Constructive overlap is a bonding MO.
- Destructive overlap is an antibonding MO.

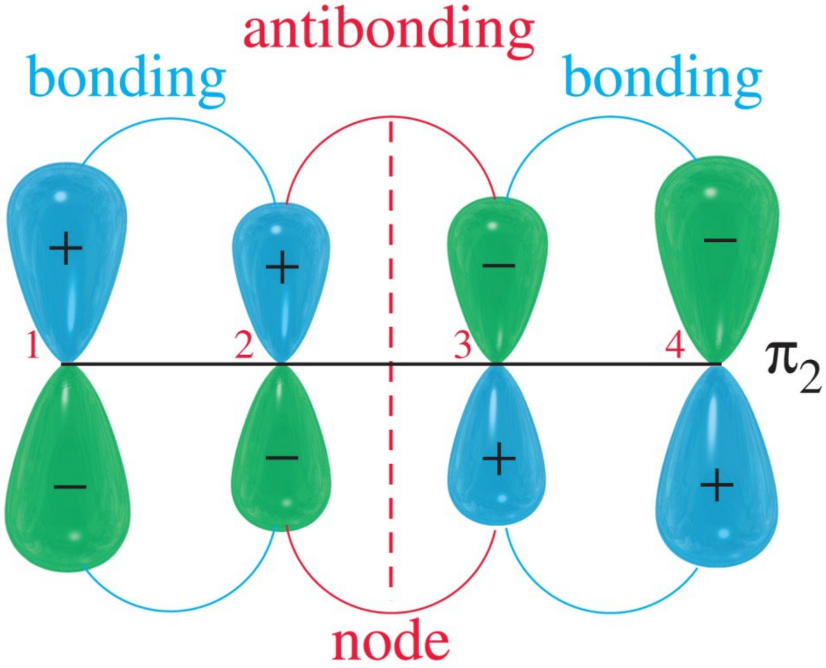
$_1$ MO for 1,3-Butadiene

- Lowest energy.
- All bonding interactions.
- Electrons are delocalized over four nuclei.



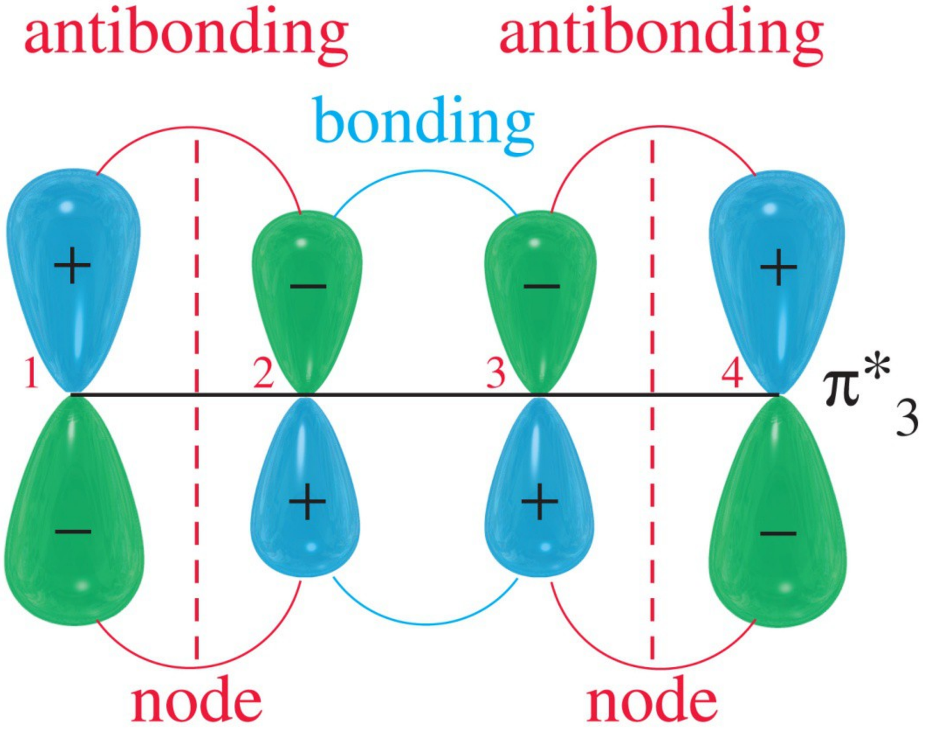
$_2$ MO for 1,3-Butadiene

- Two bonding interactions.
- One antibonding interaction.
- A bonding MO.
- Higher energy than $_1$ MO and not as strong.



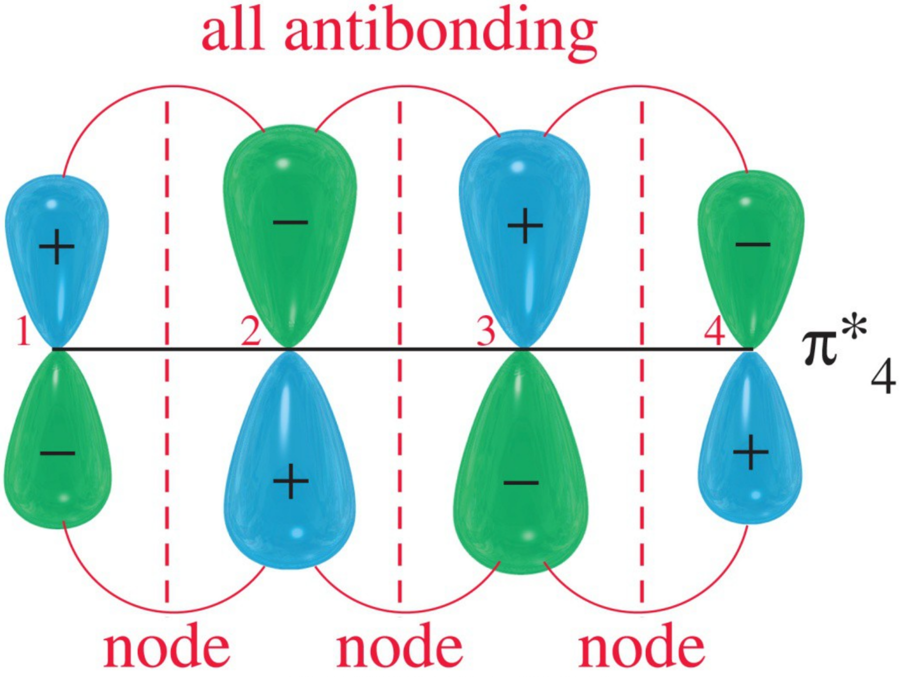
$_{3}$* MO for 1,3-Butadiene

- Antibonding MO.
- Empty at ground state.
- Two nodes.
- Vacant in the ground state.

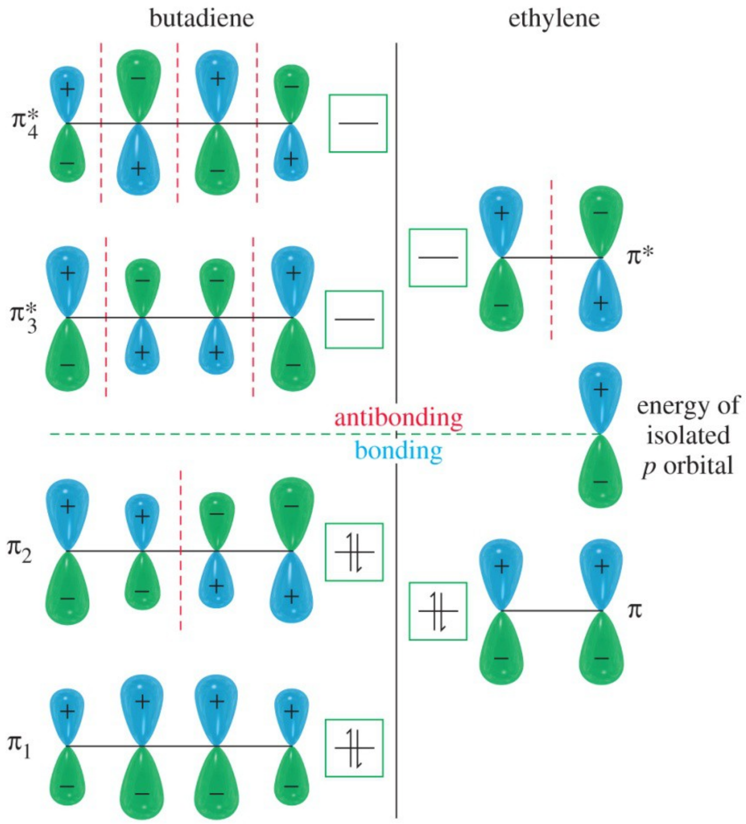


$_4$* MO for 1,3-Butadiene

- Strongly antibonding.
- Very high.
- Vacant at ground state.



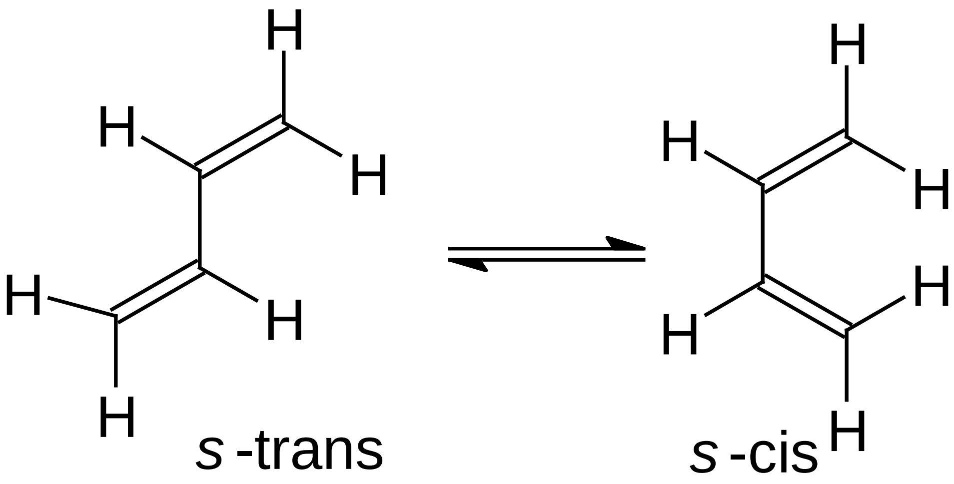
MO for 1,3-Butadiene and Ethylene



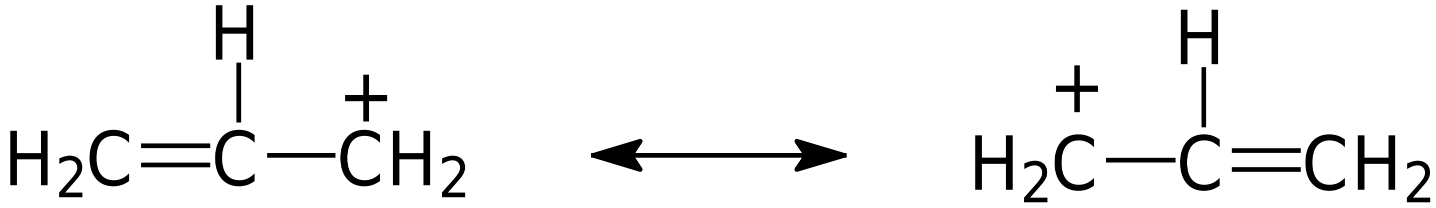
- The bonding MOs of both 1,3-butadiene and ethylene are filled and the antibonding MOs are empty.
- Butadiene has lower energy than ethylene.
- This lower energy is the resonance stabilization of the conjugated diene.

Conformations of 1,3-Butadiene

- The *s*-trans conformer is more stable than the *s*-cis by 12 kJ/mol (2.8 kcal/mol).
- Easily interconvert at room temperature.



Allylic Cations



- The positive charge is delocalized over two carbons by resonance giving the allyl cation more stability than nonconjugated cations.

Stability of Carbocations

$$H_3C^+ < 1° < 2°\text{, allyl} < 3°\text{, substituted allylic}$$

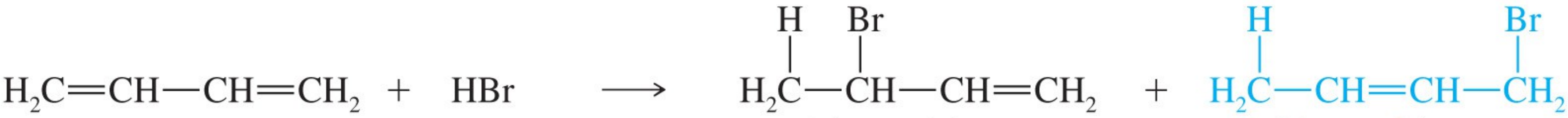
$$H_2\overset{\frac{1}{2}+}{C}{=\!=}CH{=\!=}\overset{\frac{1}{2}+}{C}H_2 \quad \text{is about as stable as} \quad CH_3—\overset{+}{C}H—CH_3$$

- Stability of 1 allylic   2 carbocation.
- Stability of 2 allylic   3 carbocation.

1,2- and 1,4-Addition to Conjugated Dienes

- Electrophilic addition to the double bond produces the most stable intermediate.
- For conjugated dienes, the intermediate is a resonance-stabilized allylic cation.
- Nucleophile adds to either Carbon 2 or 4, both of which have the delocalized positive charge.

1,2- and 1,4-Addition to Dienes



$$H_2C{=}CH{-}CH{=}CH_2 + HBr \longrightarrow H_2\overset{\overset{H}{|}}{C}{-}\overset{\overset{Br}{|}}{CH}{-}CH{=}CH_2 + H_2\overset{\overset{H}{|}}{C}{-}CH{=}CH{-}\overset{\overset{Br}{|}}{CH_2}$$

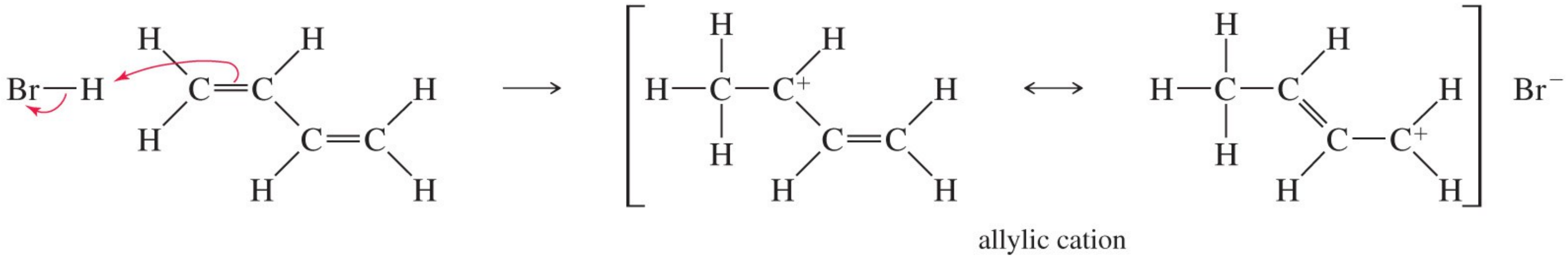
3-bromo-1-butene
1,2-addition

1-bromo-2-butene
1,4-addition

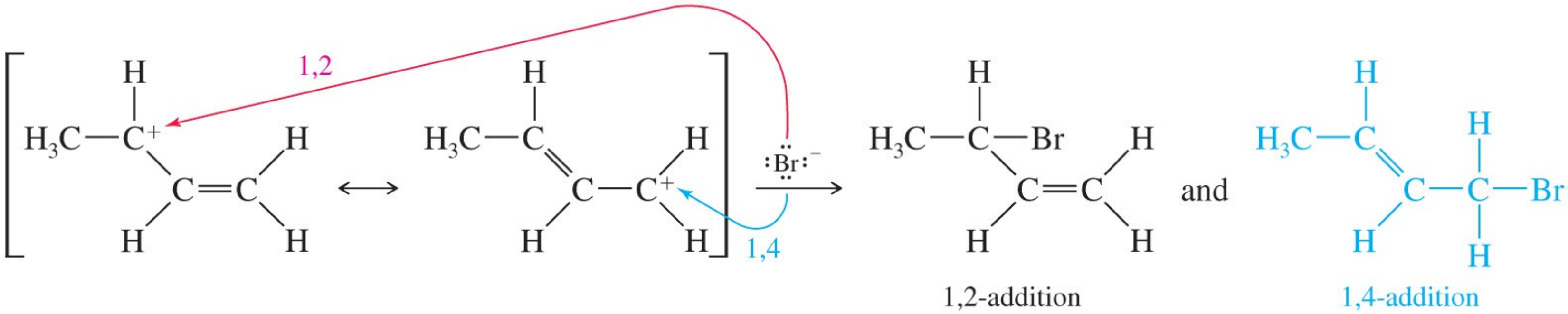
- Addition of HBr to 1,3-butadiene produces 3-bromo-1-butene (1,2-addition) and 1-bromo-2-butene (1,4-addition).

Mechanism of 1,2- and 1,4-Addition

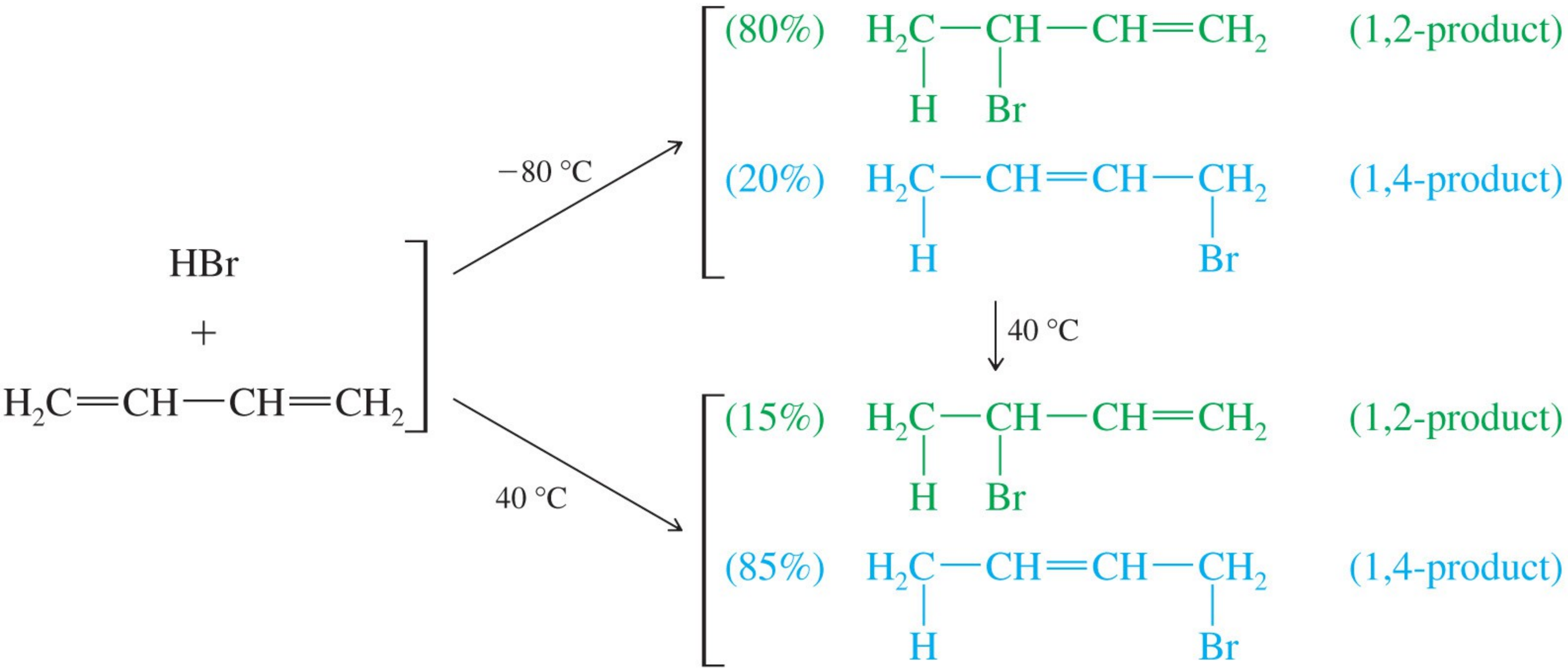
Step 1: Protonation of one of the double bonds forms a resonance-stabilized allylic cation.



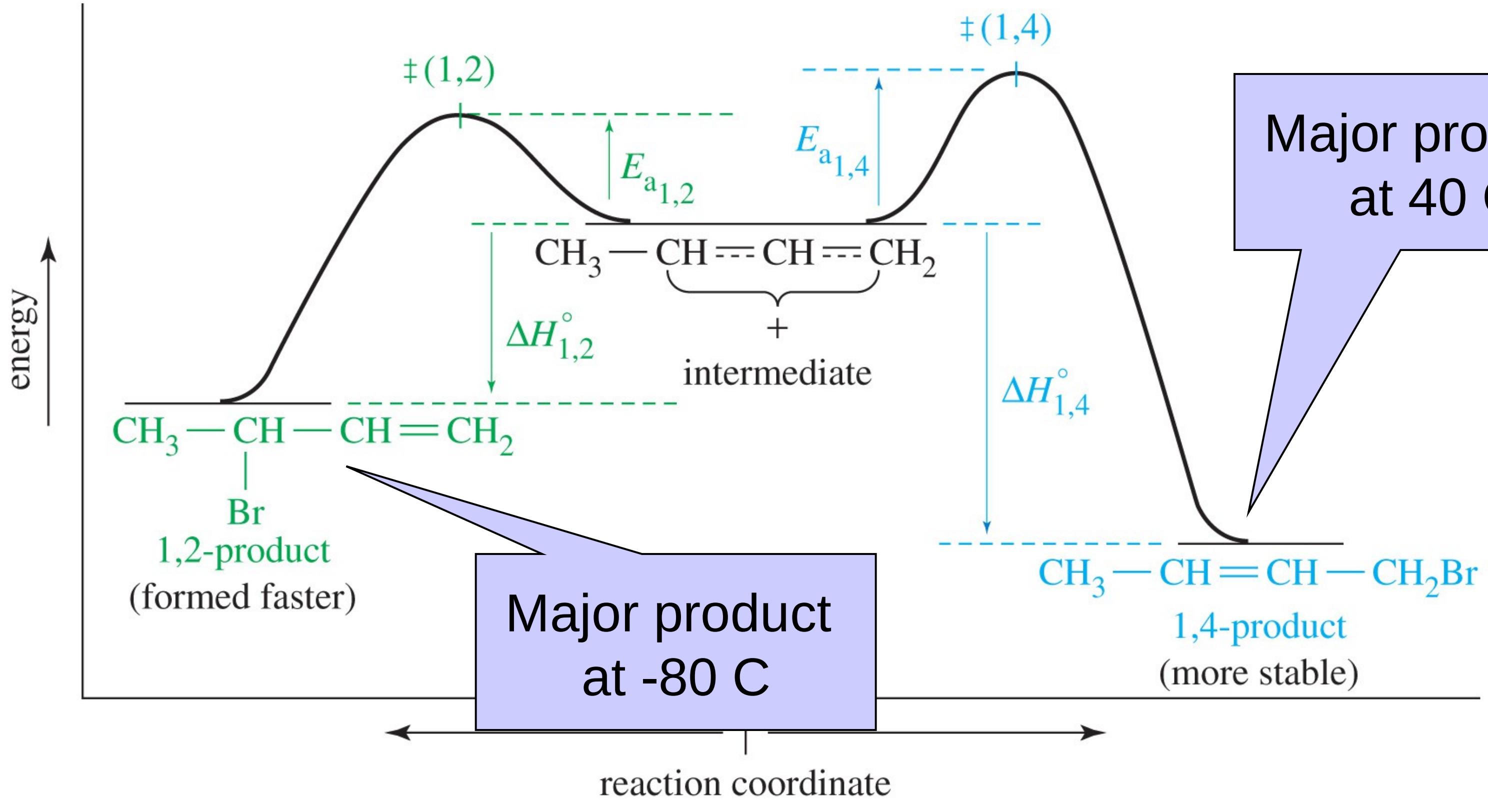
Step 2: A nucleophile attacks at either electrophilic carbon atom.



Kinetic Versus Thermodynamic Control



Kinetic Versus Thermodynamic Control (Continued)



Major product at 40 C

Major product at -80 C

Kinetic Control at -80°C

- Transition state for the 1,2-addition has a lower E_a because it is a more stable secondary carbocation.
- The 1,2-addition will be the faster addition at any temperature.
- The nucleophilic attack of the bromide on the allylic carbocation is irreversible at this low temperature.
- The product that forms faster predominates (kinetic product).
- Because the kinetics of the reaction determines the product, the reaction is said to be under ***kinetic control***.

Thermodynamic Control at 40°C

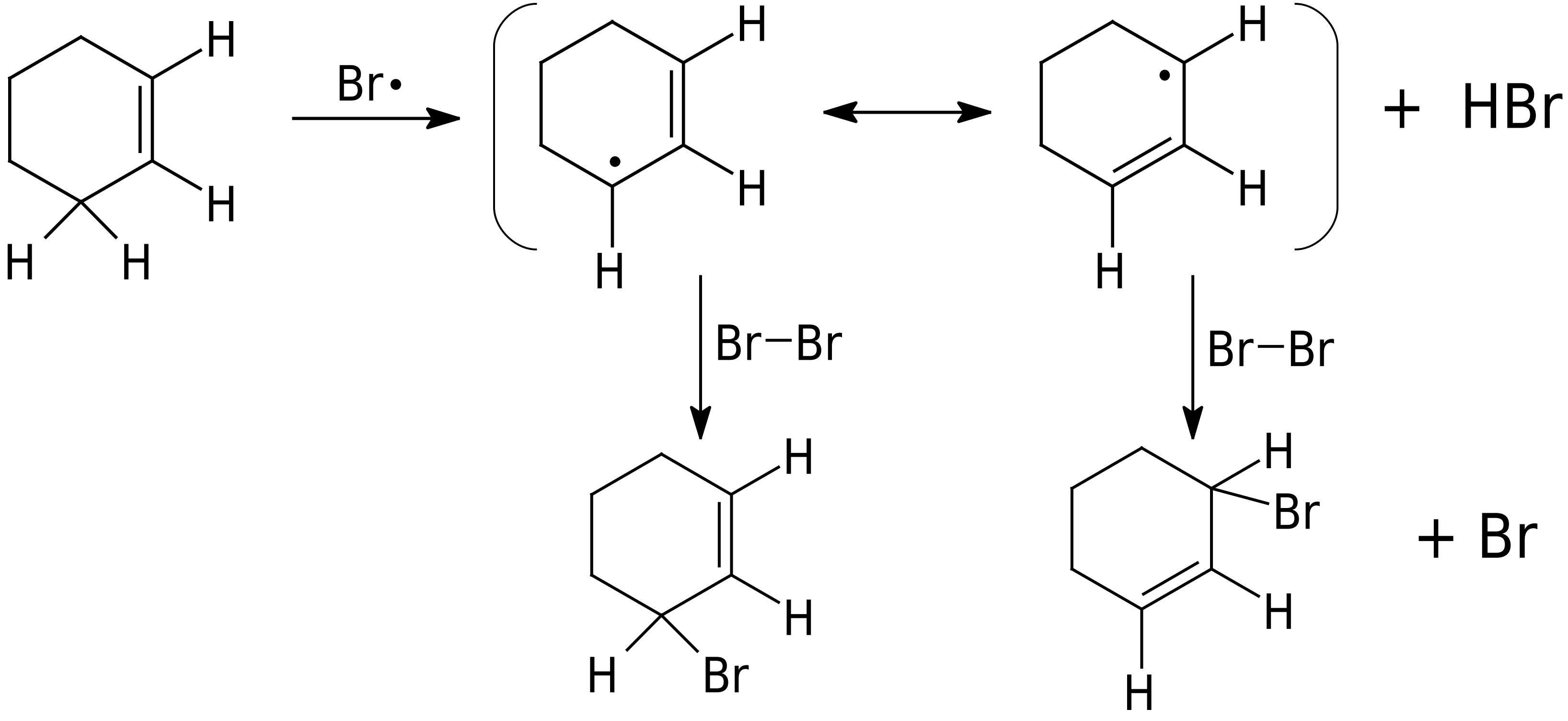
- The 1,2-addition is still the faster addition, but at 40°C, the bromide attack is reversible.
- An equilibrium is established, which favors the most stable product:
- The 1,4-addition is the most stable product (thermodynamic product) because it has a more substituted double bond.
- Because the thermodynamics of the reaction determines the product, the reaction is said to be under ***thermodynamic control***.

Allylic Radicals

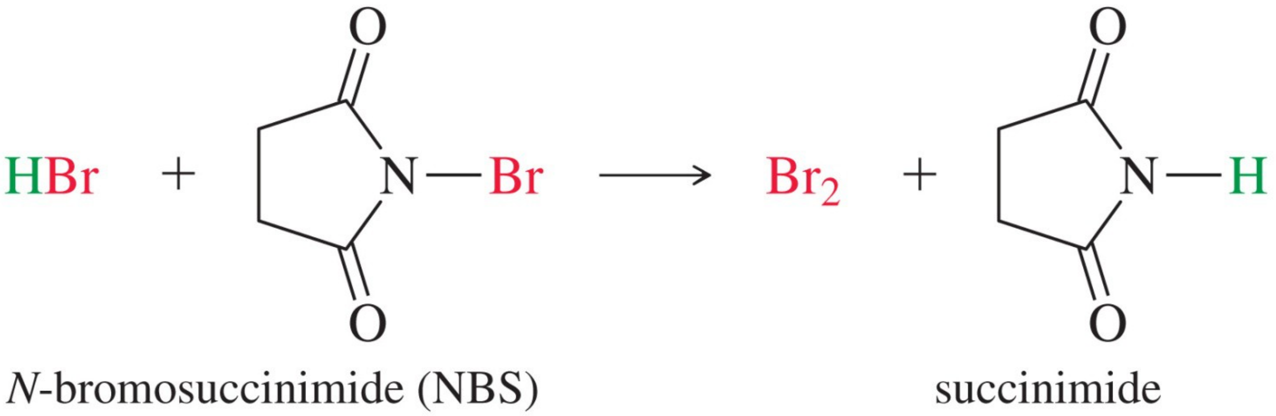
- Stabilized by resonance.
- Radical stabilities: 1 < 2 < 3 < 1 allylic.
- Substitution at the allylic position competes with addition to double bond.
- To encourage substitution, use a low concentration of reagent with light, heat, or peroxides to initiate free radical formation.

Mechanism of Allylic Bromination

$$Br_2 \xrightarrow{h} 2\ Br\bullet$$



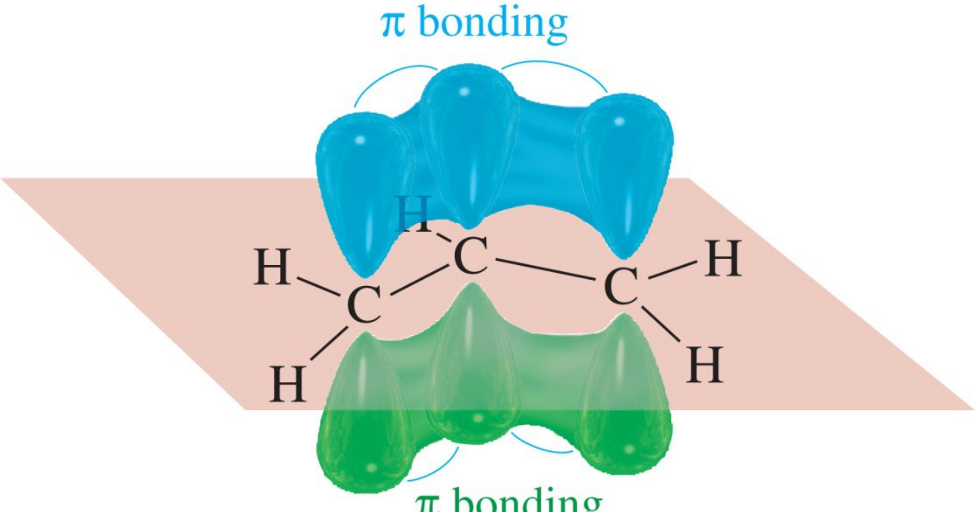
Bromination Using *N*-Bromosuccinimide (NBS)



- NBS provides a low, constant concentration of Br_2.
- NBS reacts with the HBr by-product to produce Br_2 and to prevent HBr addition across the double bond.

Allyl System

- Geometric structure of the allyl cation, allyl radical, and allyl anion.
- The three *p* orbitals of the allyl system are parallel to each other, allowing for the extended overlap between C1–C2 and C2–C3.



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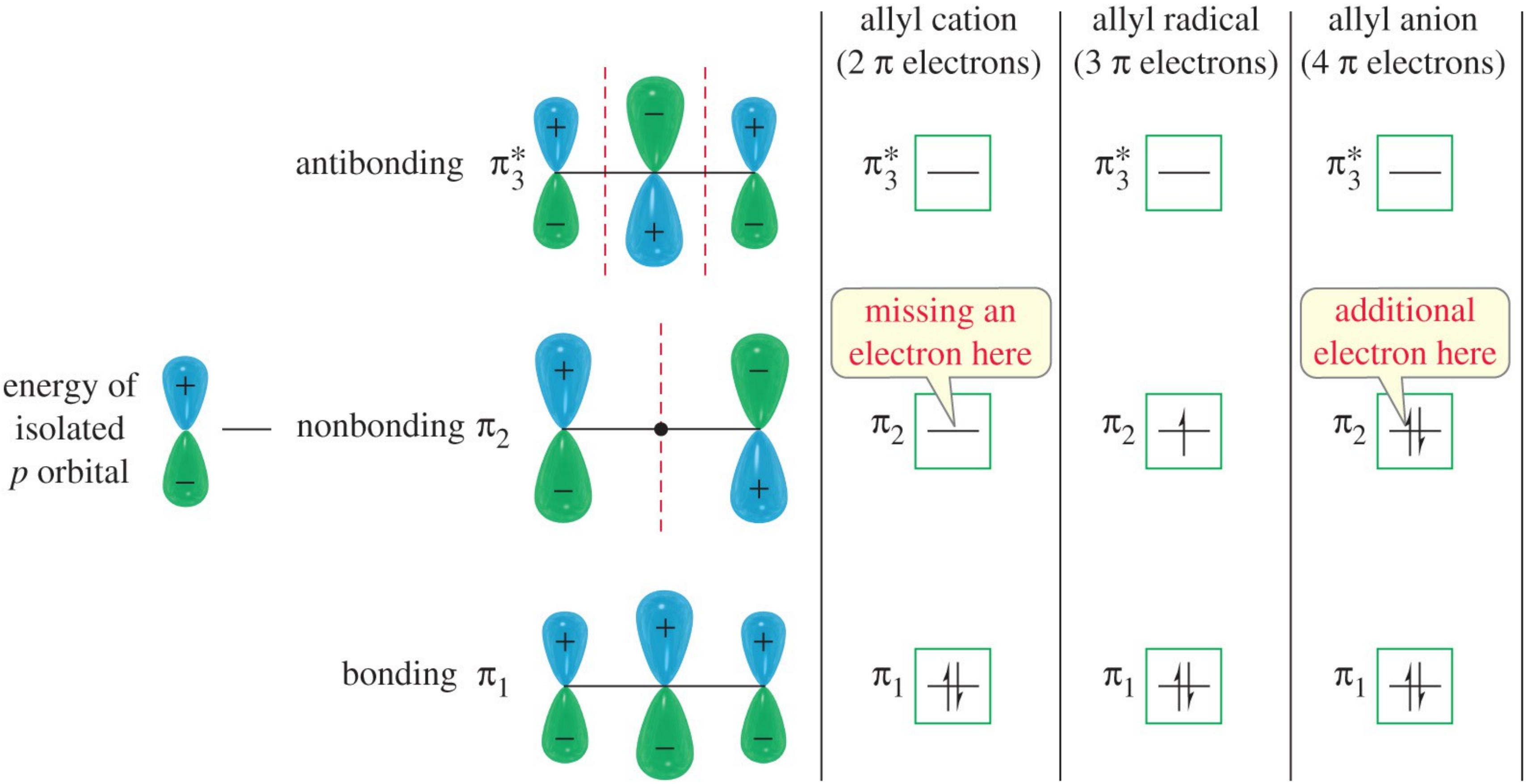
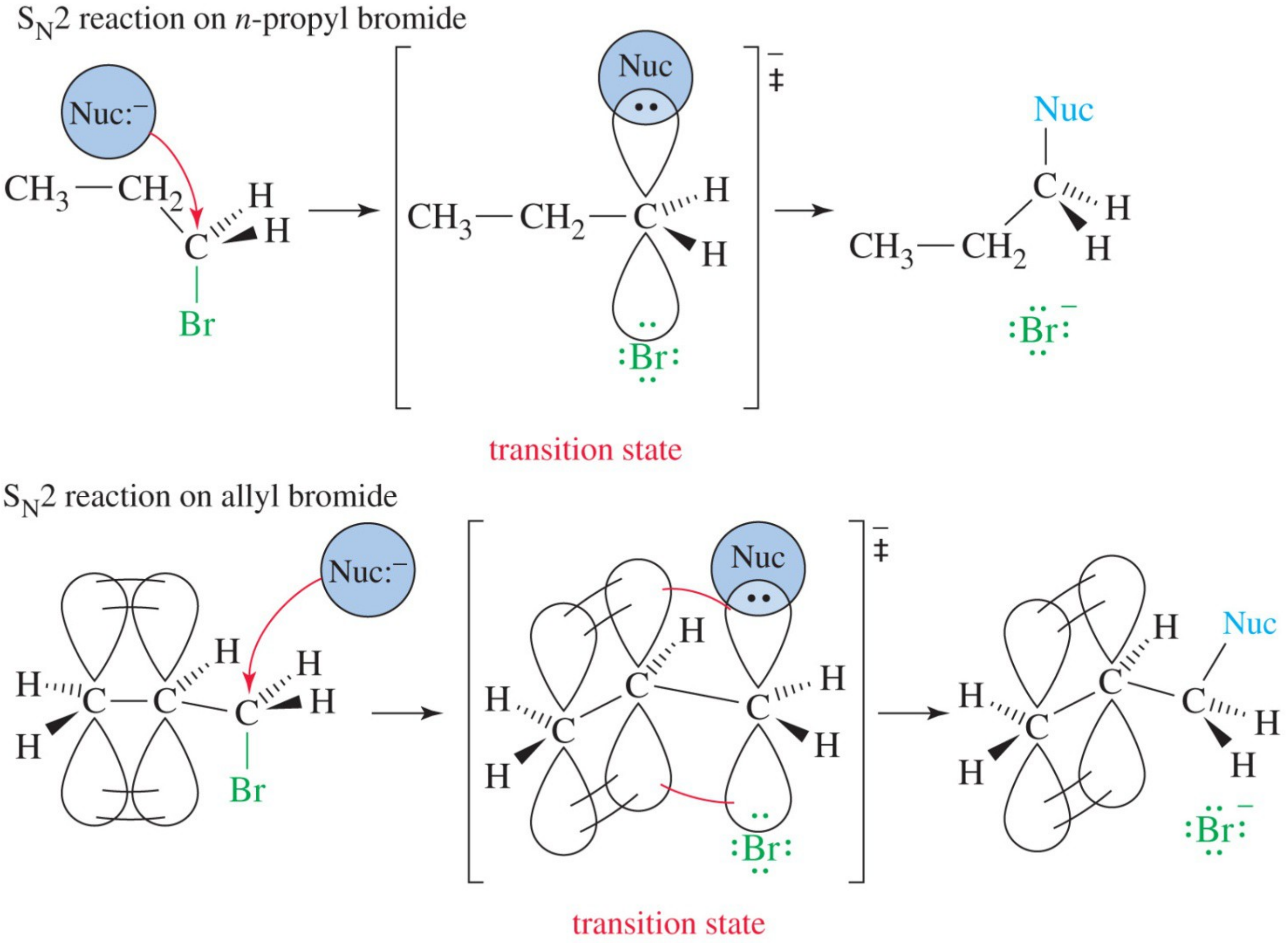
MOs for the Allylic Systems



S_N2 Reactions of Allylic Halides



S_N2 Reactions

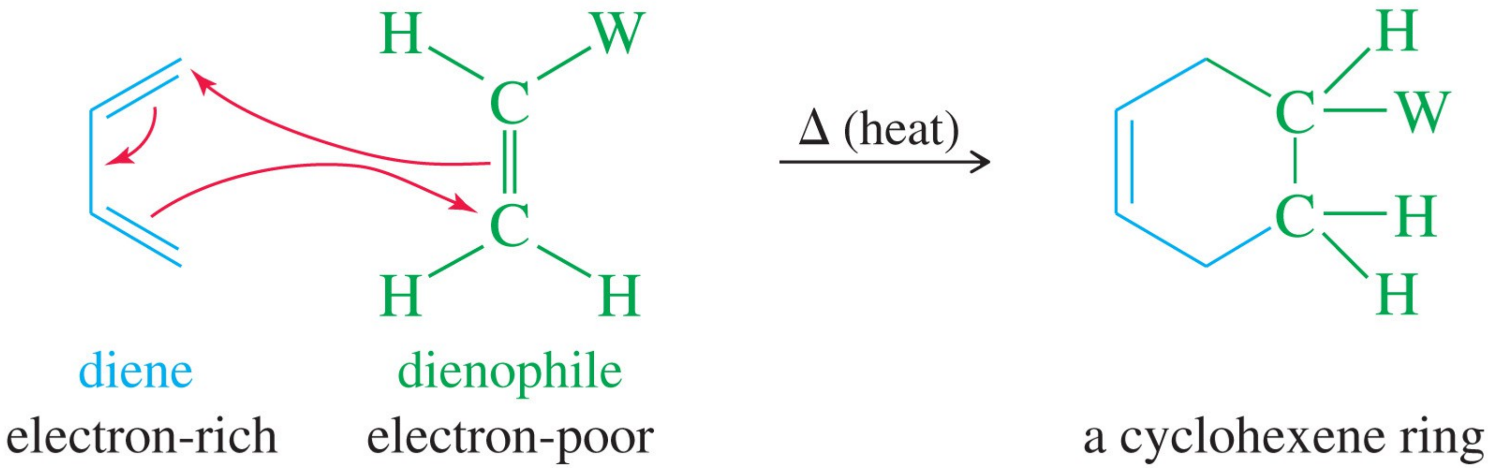
- Allylic halides and tosylates are highly reactive substrates for S_N2 reactions.
- The transition state is stabilized through conjugation with the *p* orbitals of the pi bond.
- Allylic halides and tosylates react with Grignards and organolithiums:

$$H_2C{=}CHCH_2Br + CH_3Li \rightarrow H_2C{=}CHCH_2CH_3 + LiBr$$

Diels–Alder Reaction

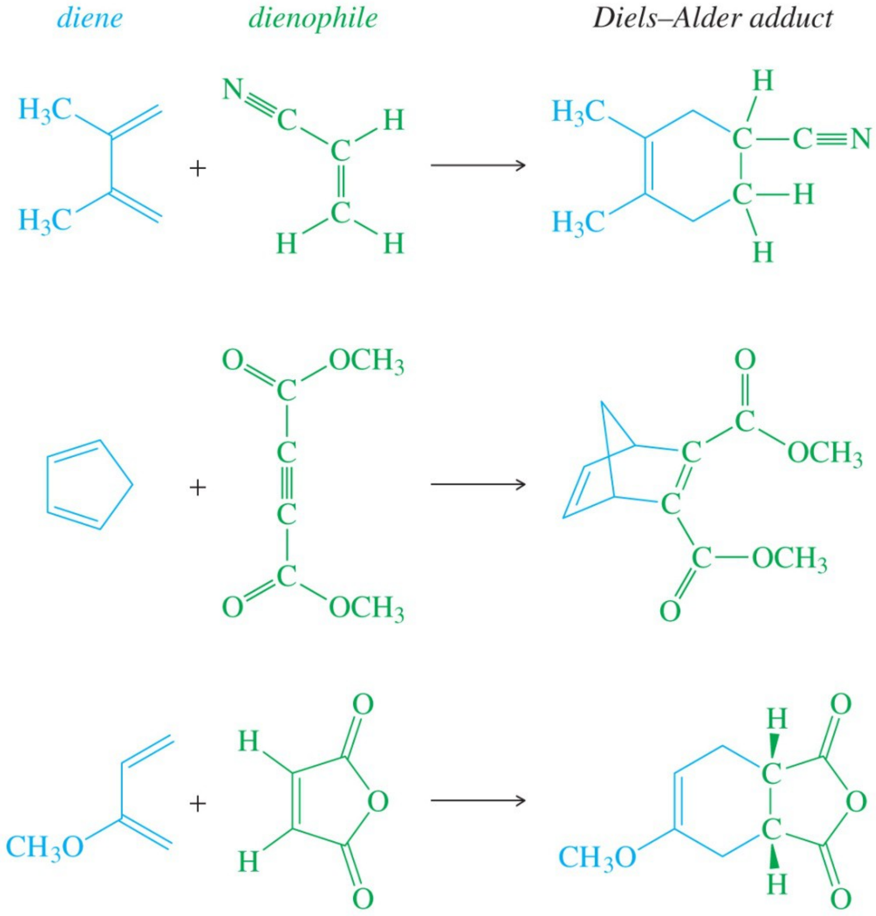
- Named after Otto Diels and Kurt Alder. They received the Nobel prize in1950.
- Produces a cyclohexene ring.
- The reaction is between a diene with an electron-deficient alkene (dienophile).
- The Diels-Alder is also called a [4+2] cycloaddition because a ring is formed by the interaction of four pi electrons of the alkene with two pi electrons of the alkene or alkyne.

Mechanism of the Diels–Alder Reaction



- One-step, concerted mechanism.
- A diene reacts with an electron-poor alkene (dienophile) to give cyclohexene or cyclohexadiene rings.

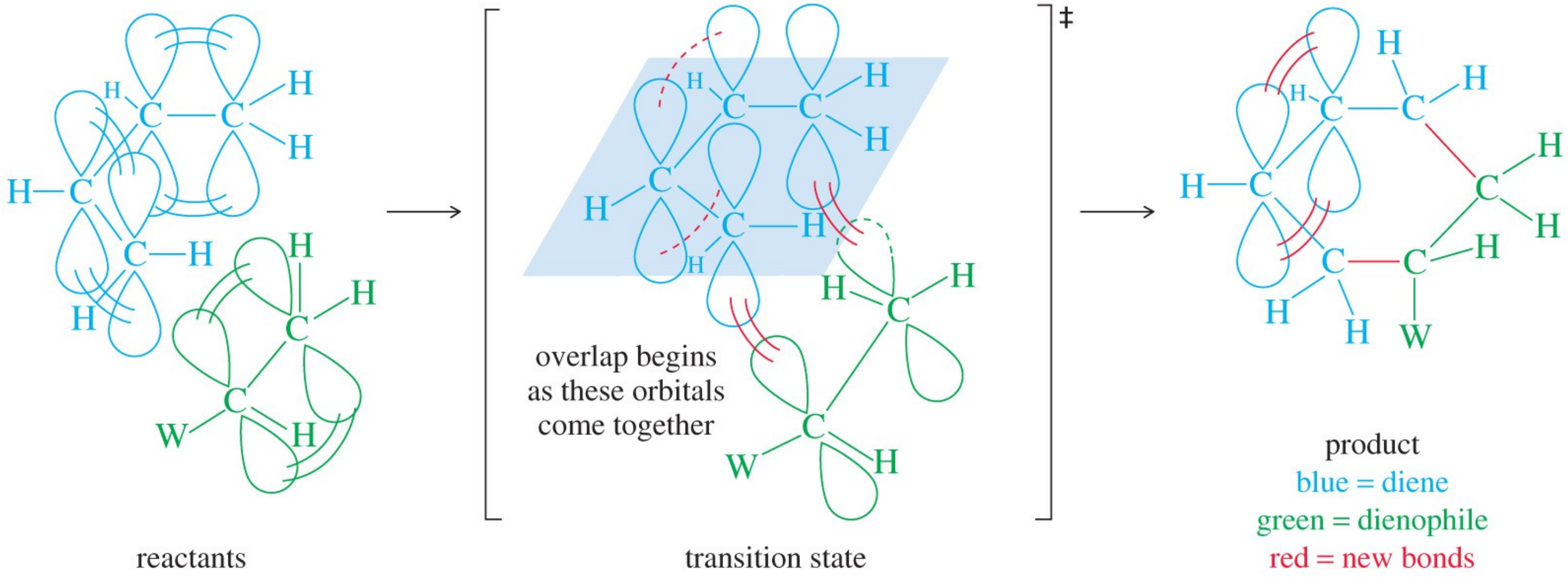
Examples of Diels–Alder Reactions



Stereochemical Requirements

- Diene must be in *s*-cis conformation.
- Diene's C1 and C4 *p* orbitals must overlap with dienophile's *p* orbitals to form new sigma bonds.
- Both sigma bonds are on same face of the diene: syn stereochemistry.

Orbital Overlap of the Diels–Alder Reaction



reactants

overlap begins as these orbitals come together

transition state

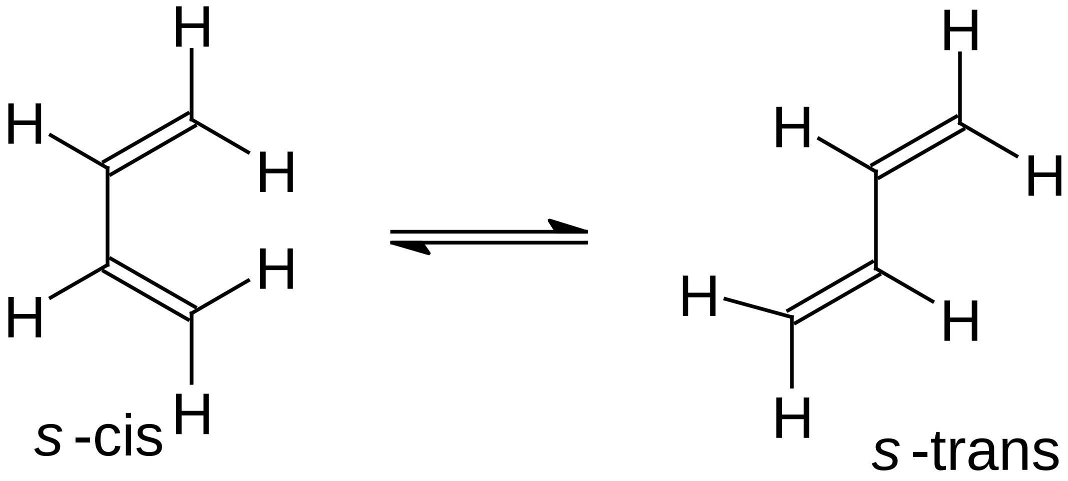
product

blue = diene

green = dienophile

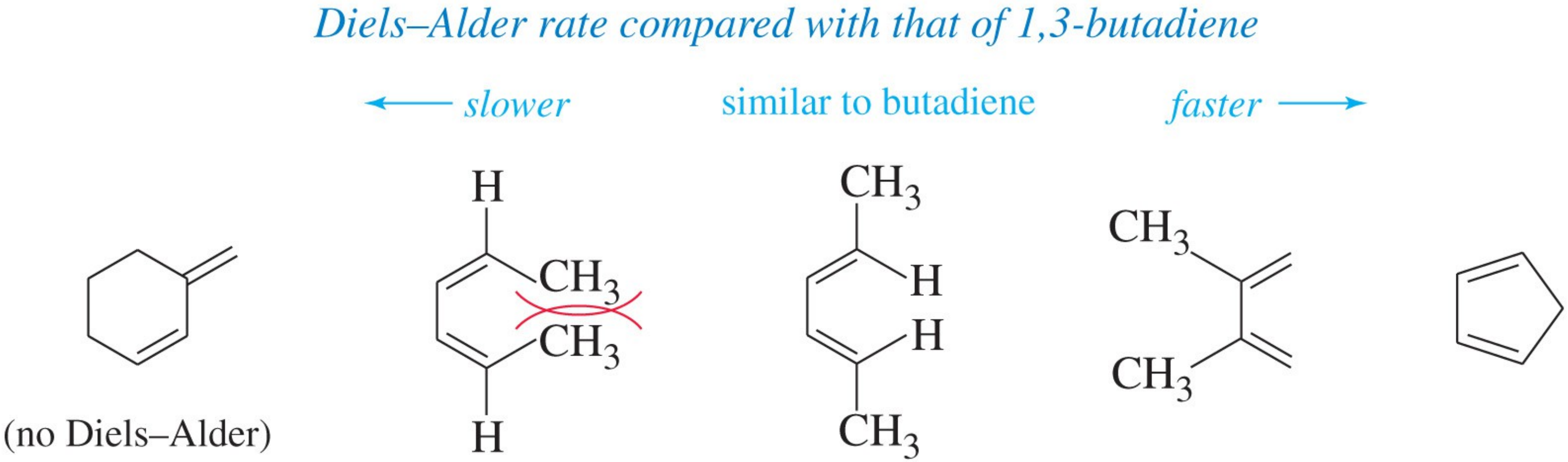
red = new bonds

S-Cis Conformation of the Diene



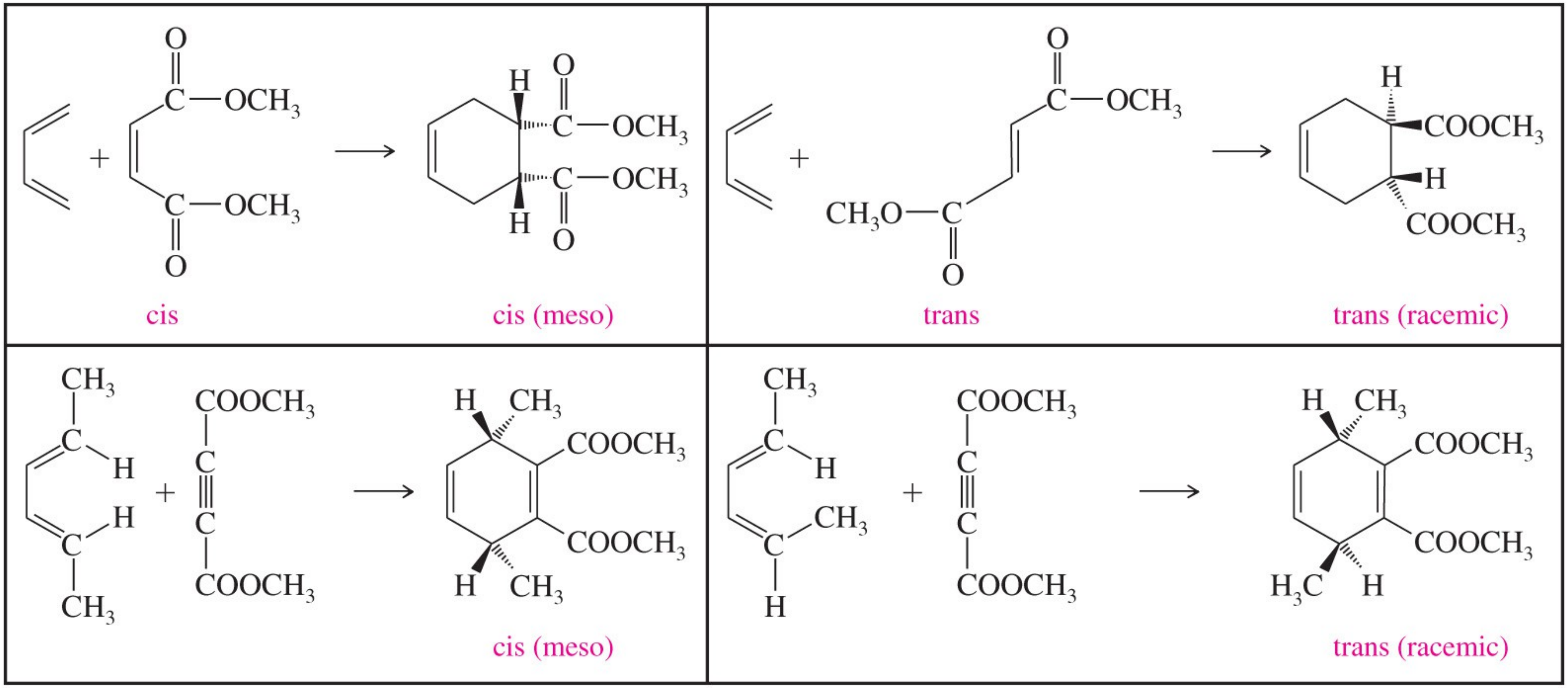
- The *s*-cis conformation can rotate around the C—C single bond to get the more stable *s*-trans conformation.
- The *s*-trans conformation is 12 kJ/mol more stable than the *s*-cis.

Diels–Alder Rate for Dienes

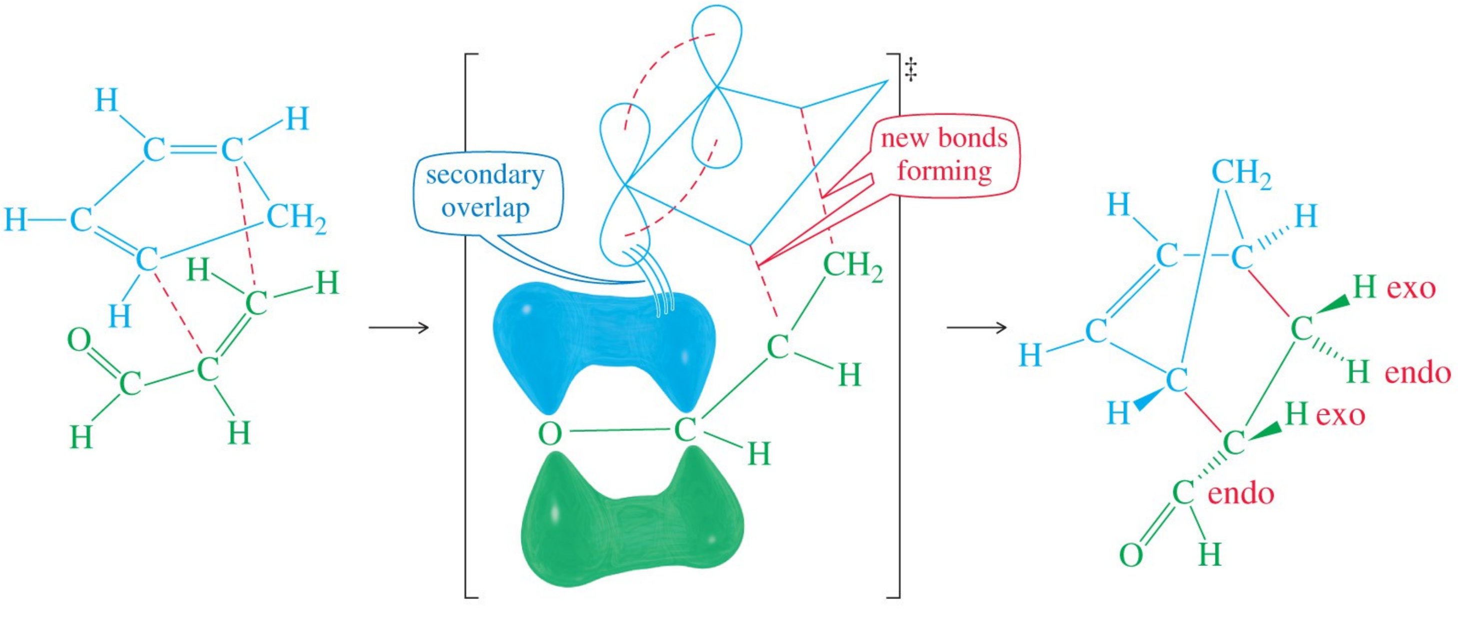


- Cyclopentadiene undergoes the Diels–Alder reaction readily because of its fixed *s*-cis conformation.
- When the diene is sterically hindered, the reaction slows down even though the conformation can be *s*-cis.
- *S*-trans dienes cannot undergo the Diels–Alder reaction.

Stereochemistry of the Diels–Alder Reaction



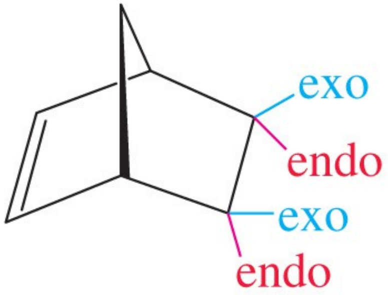
Endo Rule



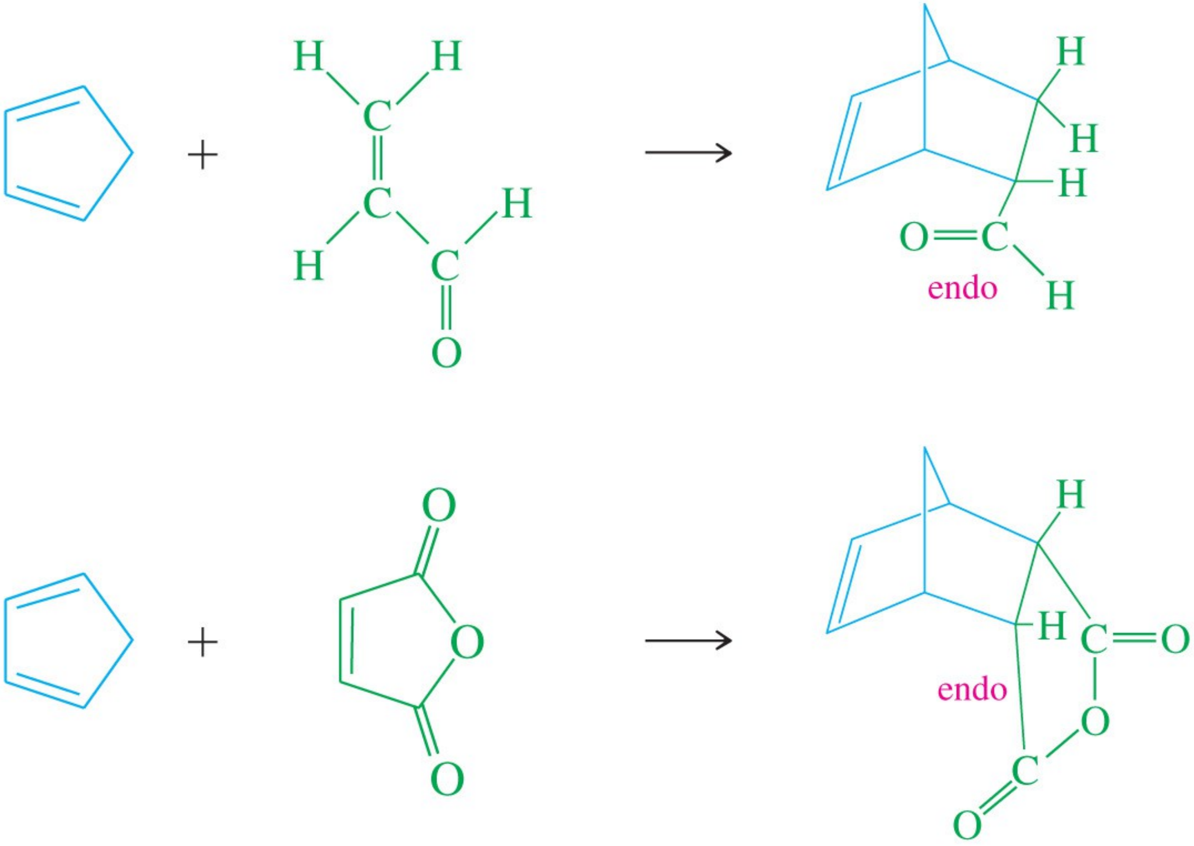
transition state

- The *p* orbitals of the electron-withdrawing groups on the dienophile have a secondary overlap with the *p* orbitals of C2 and C3 in the diene.

Examples of Endo Rule

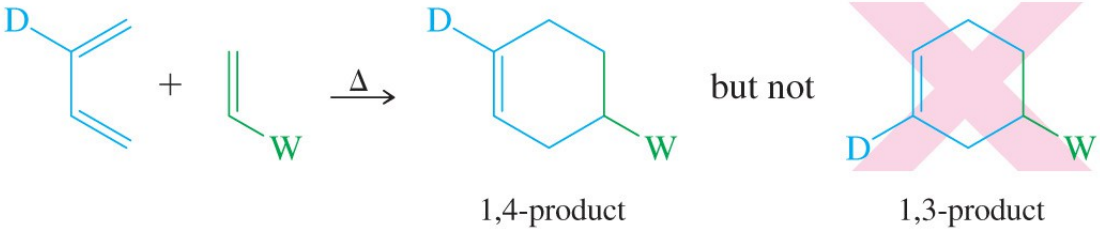


stereochemical positions of norbornene

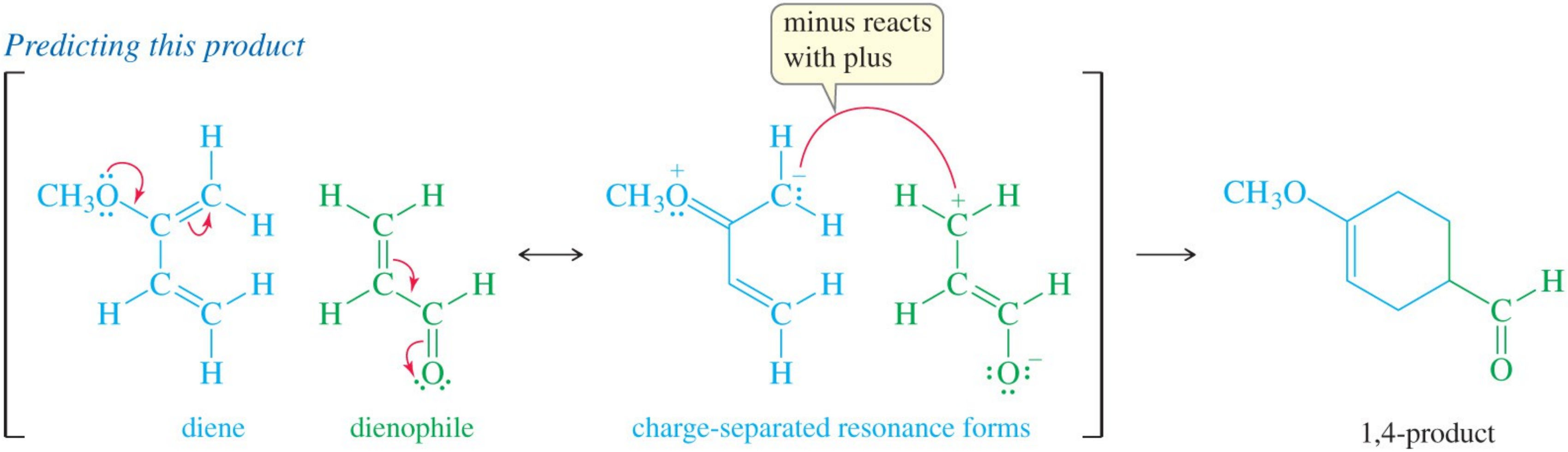


Unsymmetrical Reagents: 1,4-Product

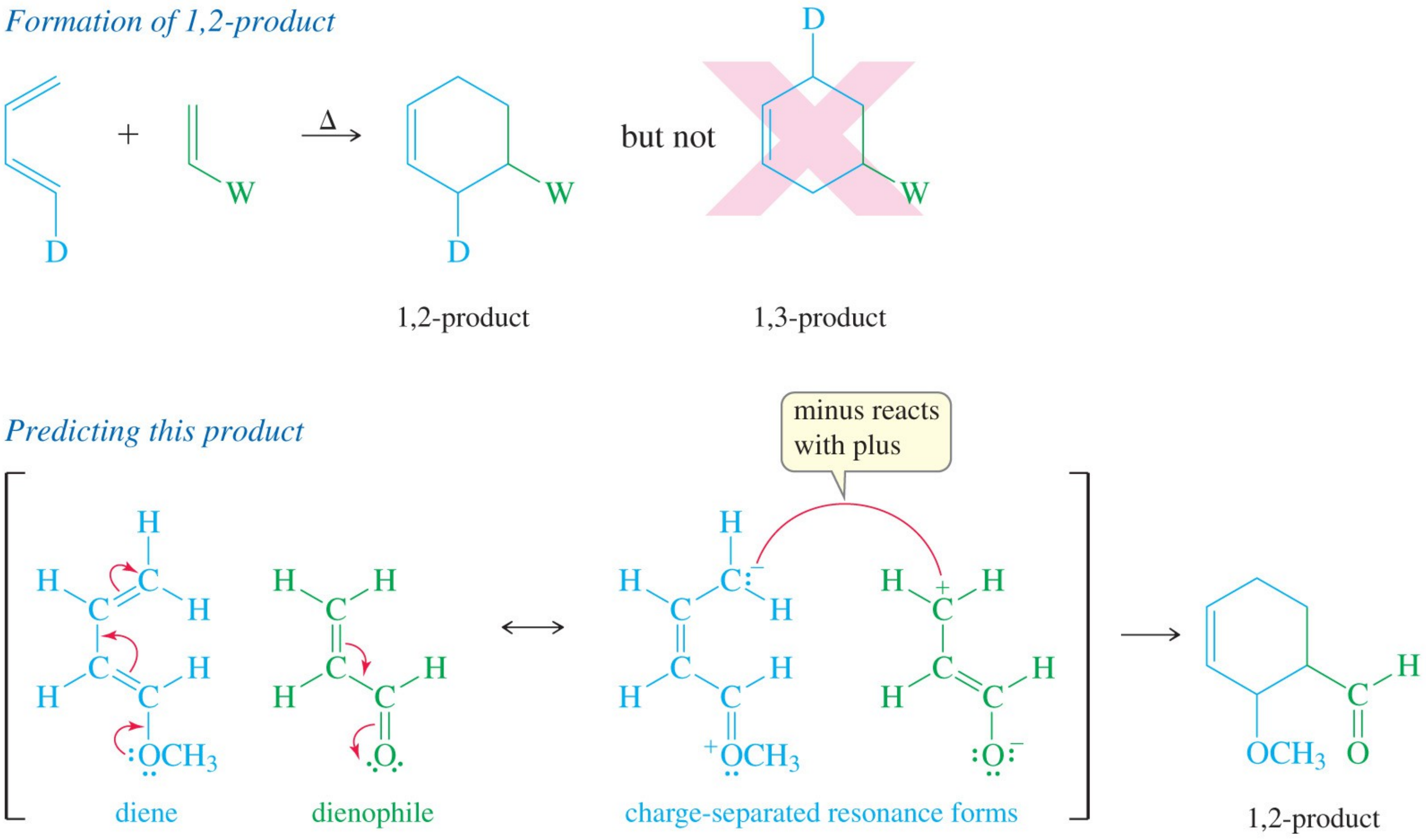
Formation of 1,4-product



Predicting this product



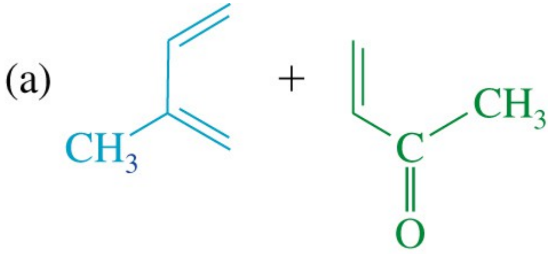
Unsymmetrical Reagents: 1,2-Product


Formation of 1,2-product

Predicting this product

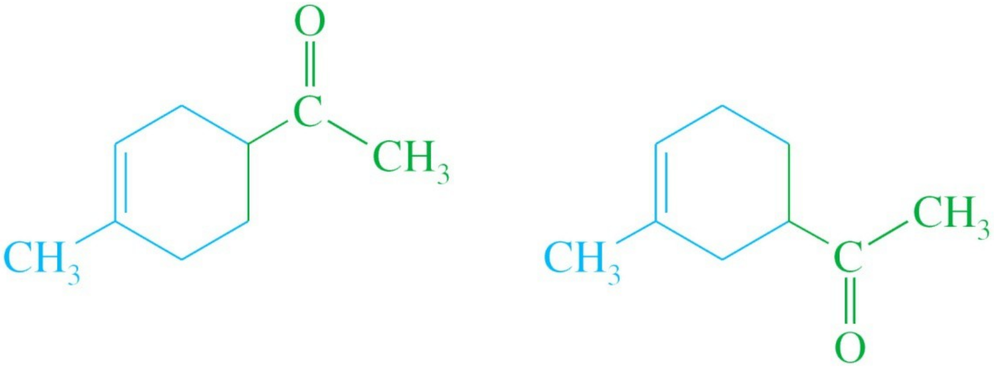
Solved Problem 1

Predict the products of the following proposed Diels–Alder reactions.



Solution

(a) The methyl group is weakly electron-donating to the diene, and the carbonyl group is electron-withdrawing from the dienophile. The two possible orientations place these groups in a 1,4-relationship or a 1,3-relationship. We select the 1,4-relationship for our predicted product. (Experimental results show a 70:30 preference for the 1,4-product.)



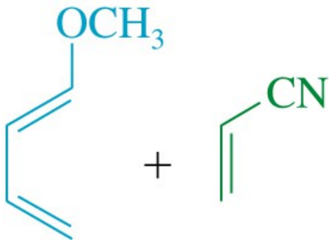
1,4-relationship (major)
(70%)

1,3-relationship (minor)
(30%)

Solved Problem 1 (Continued)

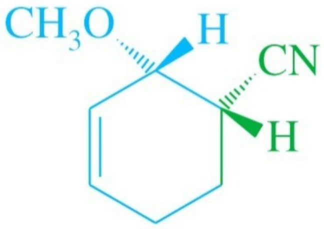
Predict the products of the following proposed Diels–Alder reactions.

(b)

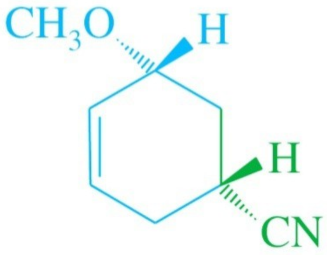


Solution (Continued)

(b) The methoxyl group $(-\mathrm{OCH_3})$ is strongly electron-donating to the diene, and the cyano group $(-\mathrm{C{\equiv}N})$ is electron-withdrawing from the dienophile. Depending on the orientation of addition, the product has either a 1,2- or a 1,3-relationship of these two groups. We select the 1,2-relationship, and the endo rule predicts cis stereochemistry of the two substituents.



1,2-relationship (product)

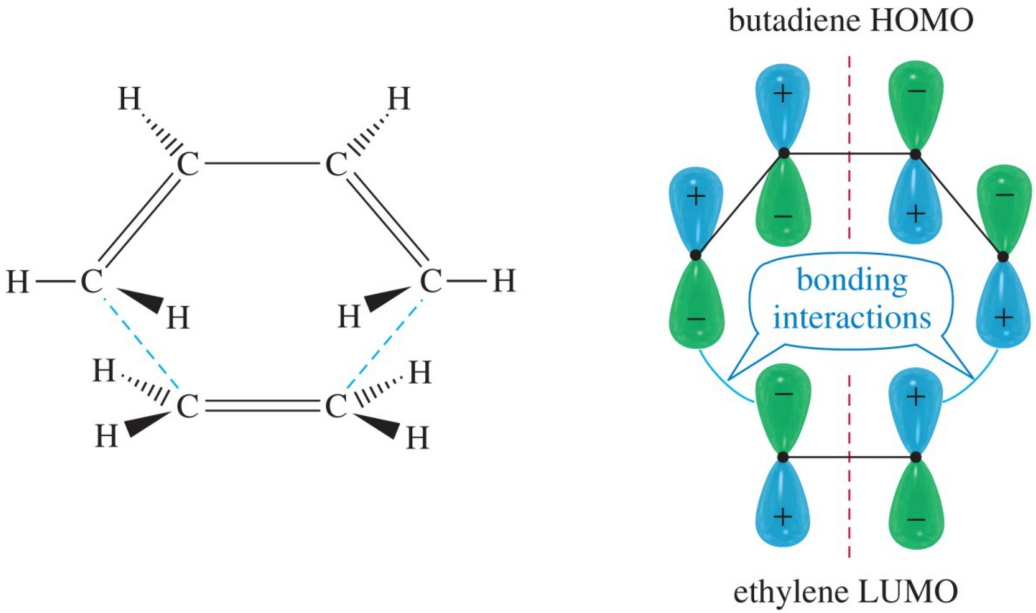


1,3-relationship (not formed)

Pericyclic Reactions

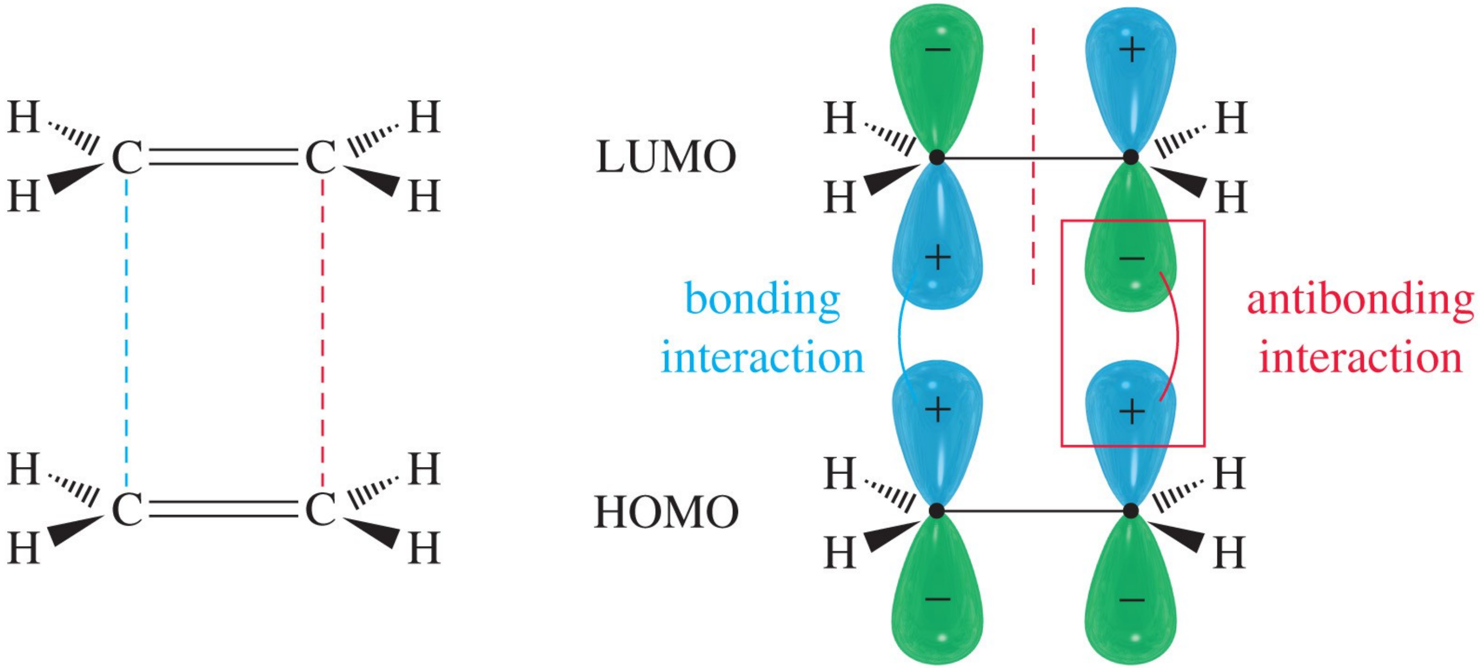
- Diels–Alder reaction is an example of a pericyclic reaction.
- Woodward and Hoffmann predicted reaction products using their theory of conservation of orbital symmetry.
- MOs must overlap constructively to stabilize the transition state.

Symmetry-Allowed Reaction



- Diene contributes electrons from its highest energy occupied orbital (HOMO).
- Dienophile receives electrons in its lowest energy unoccupied orbital (LUMO).

“Forbidden” Cycloaddition



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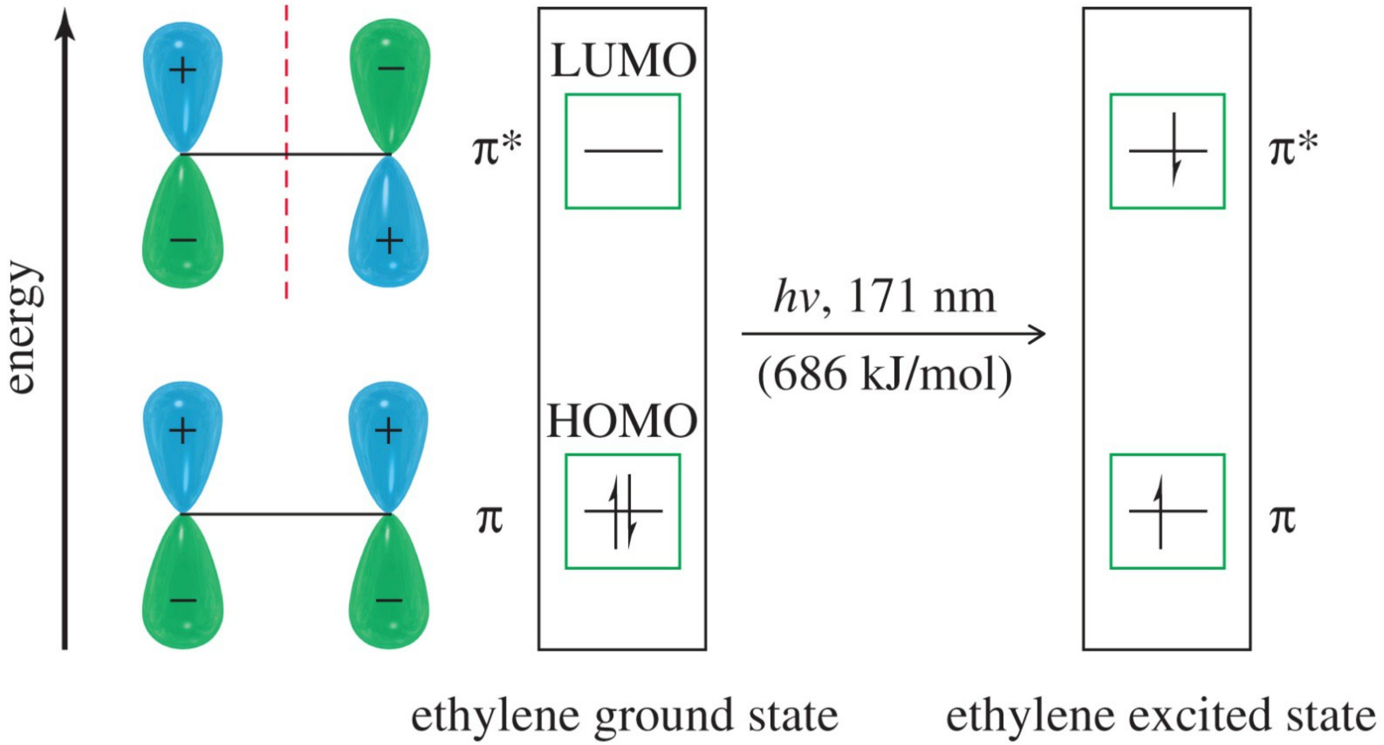
- [2 + 2] cycloaddition of two ethylenes to form cyclobutene has antibonding overlap of HOMO and LUMO.

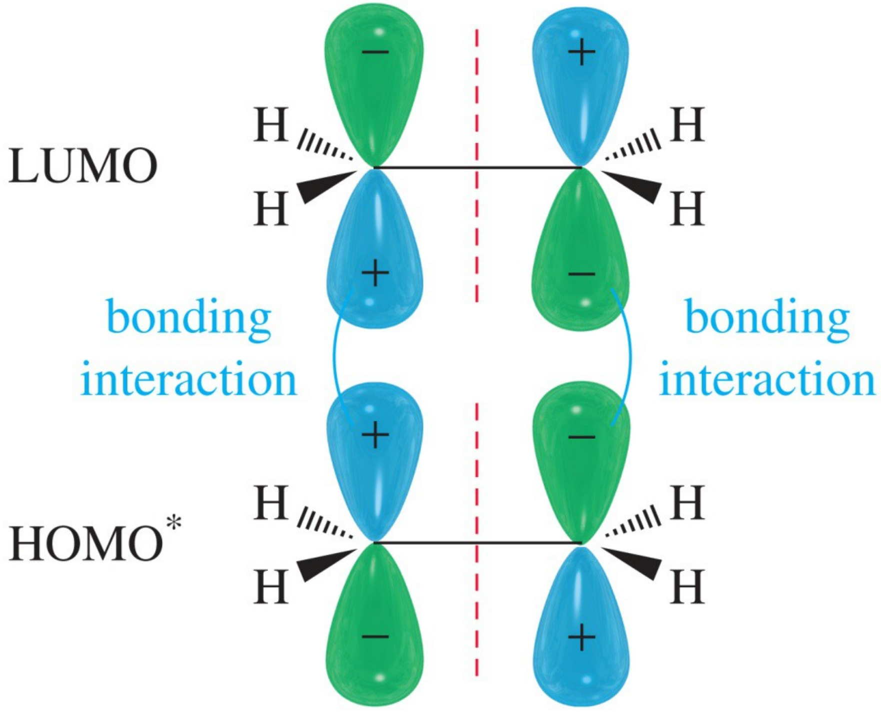
Photochemical Induction



- Absorption of correct energy photon will promote an electron to an energy level that was previously unoccupied.

[2 + 2] Cycloaddition

Photochemically allowed, but thermally forbidden.



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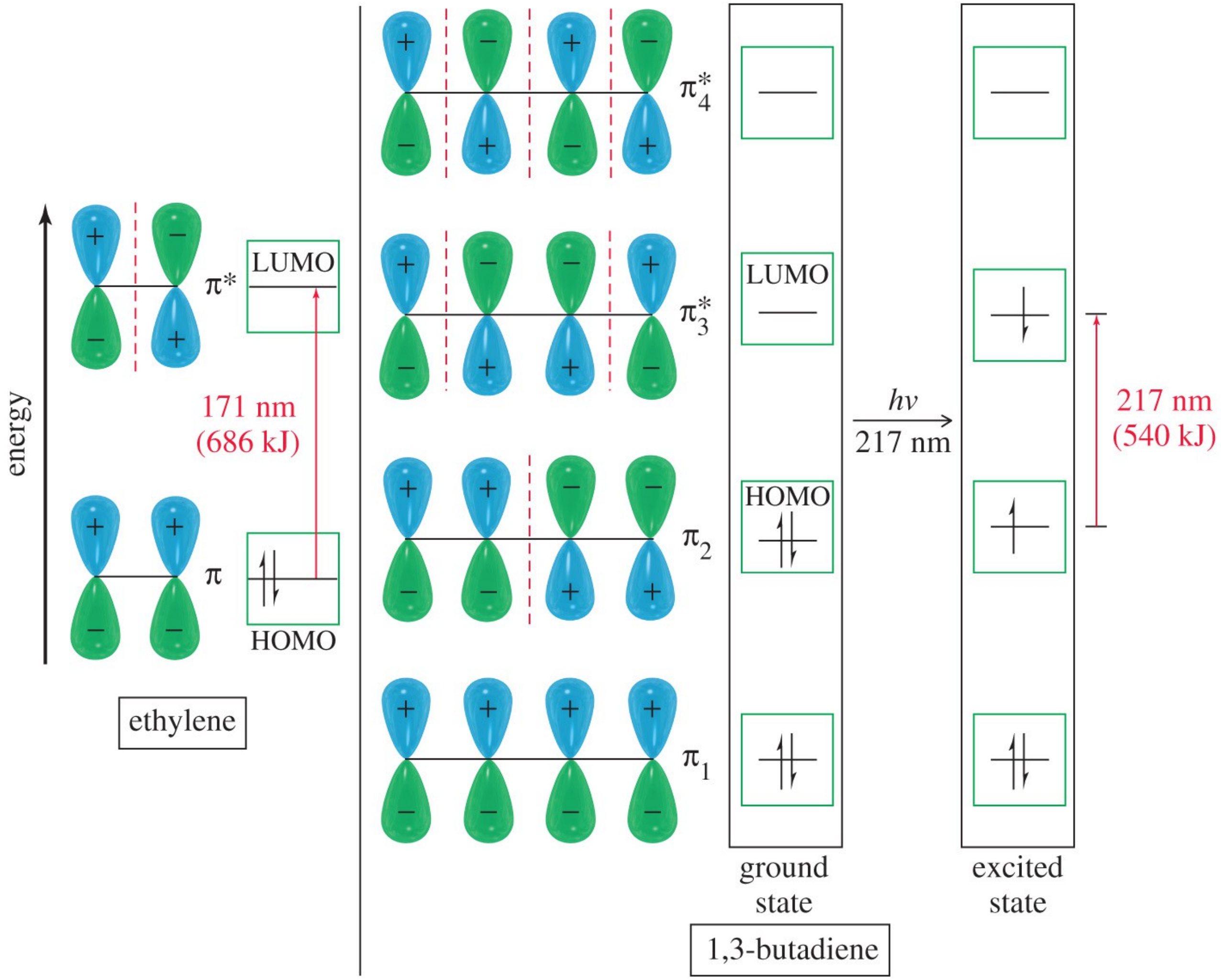
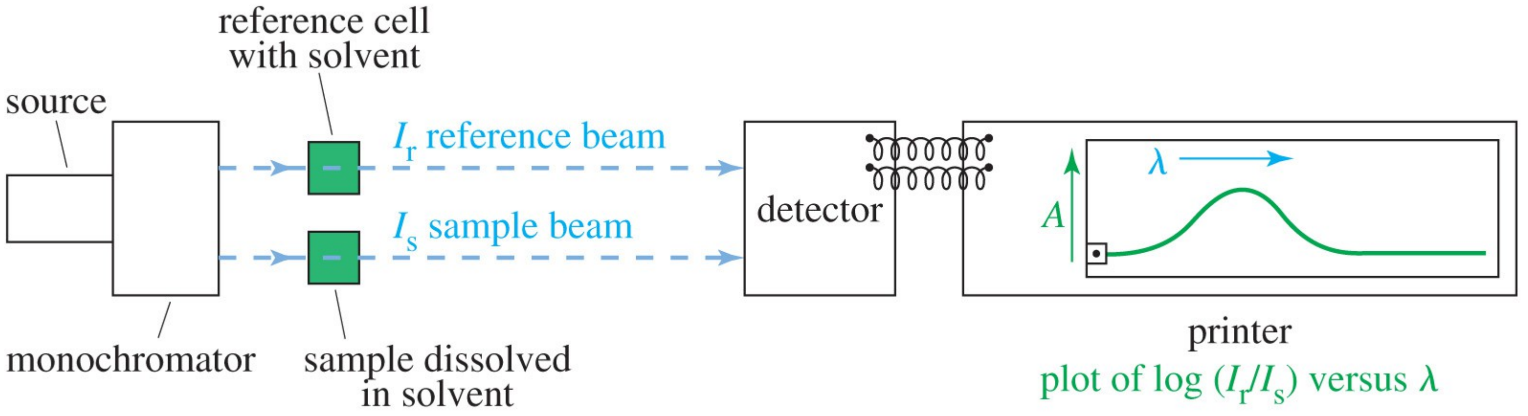
Ultraviolet Spectroscopy

- 200–400 nm photons excite electrons from a bonding orbital to a * antibonding orbital.
- Conjugated dienes have MOs that are closer in energy.
- A compound that has a longer chain of conjugated double bonds absorbs light at a longer wavelength.

* for Ethylene and Butadiene



Obtaining a UV Spectrum



- The spectrometer measures the intensity of a reference beam through solvent only ($\boldsymbol{I}_\mathrm{r}$) and the intensity of a beam through a solution of the sample ($\boldsymbol{I}_\mathrm{s}$).
- Absorbance is the log of the ratio $\boldsymbol{I}_\mathrm{r}/\boldsymbol{I}_\mathrm{s}$

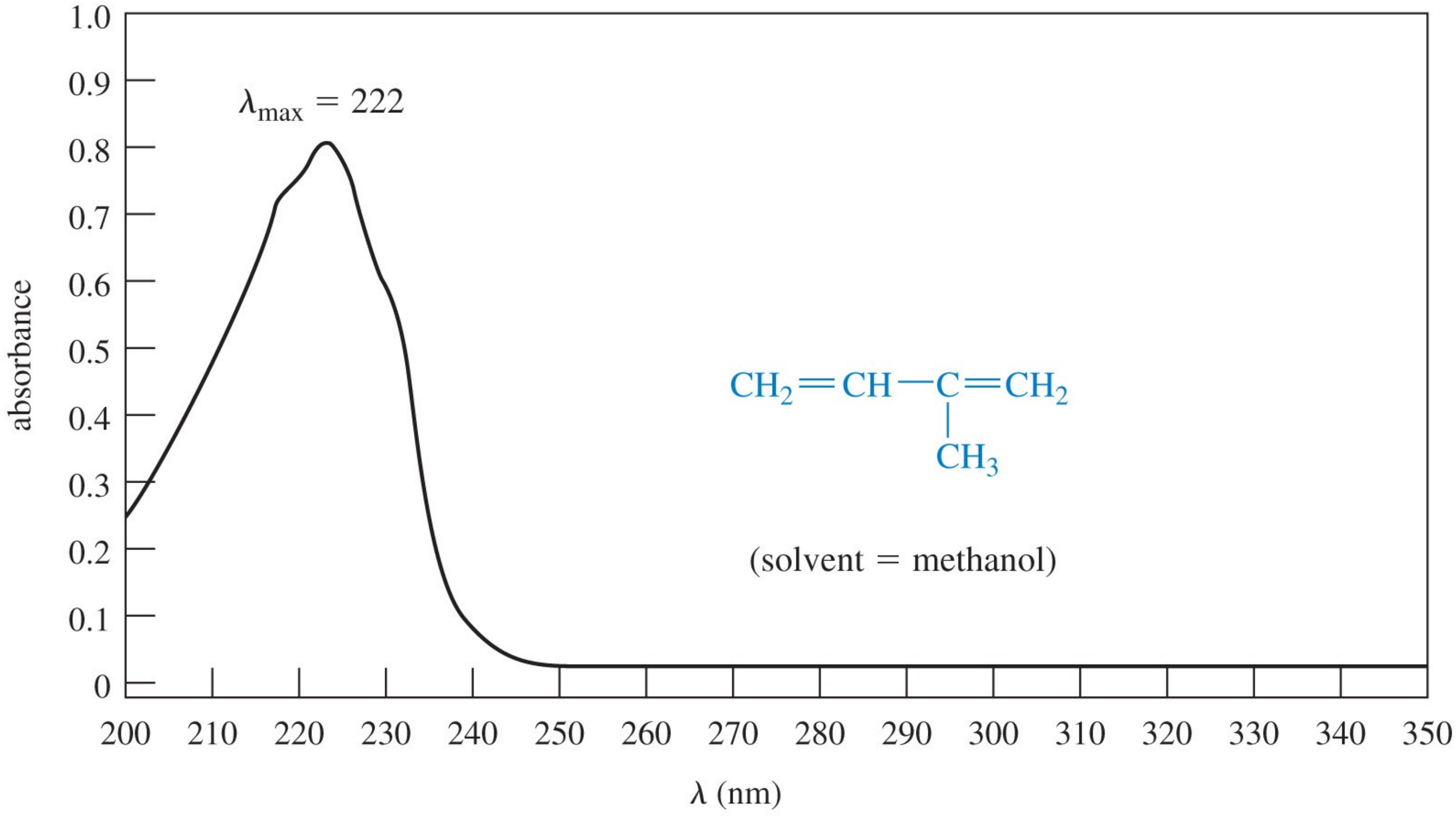
The UV Spectrum

- Usually shows broad peaks.
- Read $_{max}$ from the graph.
- Absorbance, *A*, follows Beer's Law:

$$A = cl$$

where is the molar absorptivity, *c* is the sample concentration in moles per liter, and *l* is the length of the light path in centimeters.

UV Spectrum of Isoprene



Sample UV Absorptions

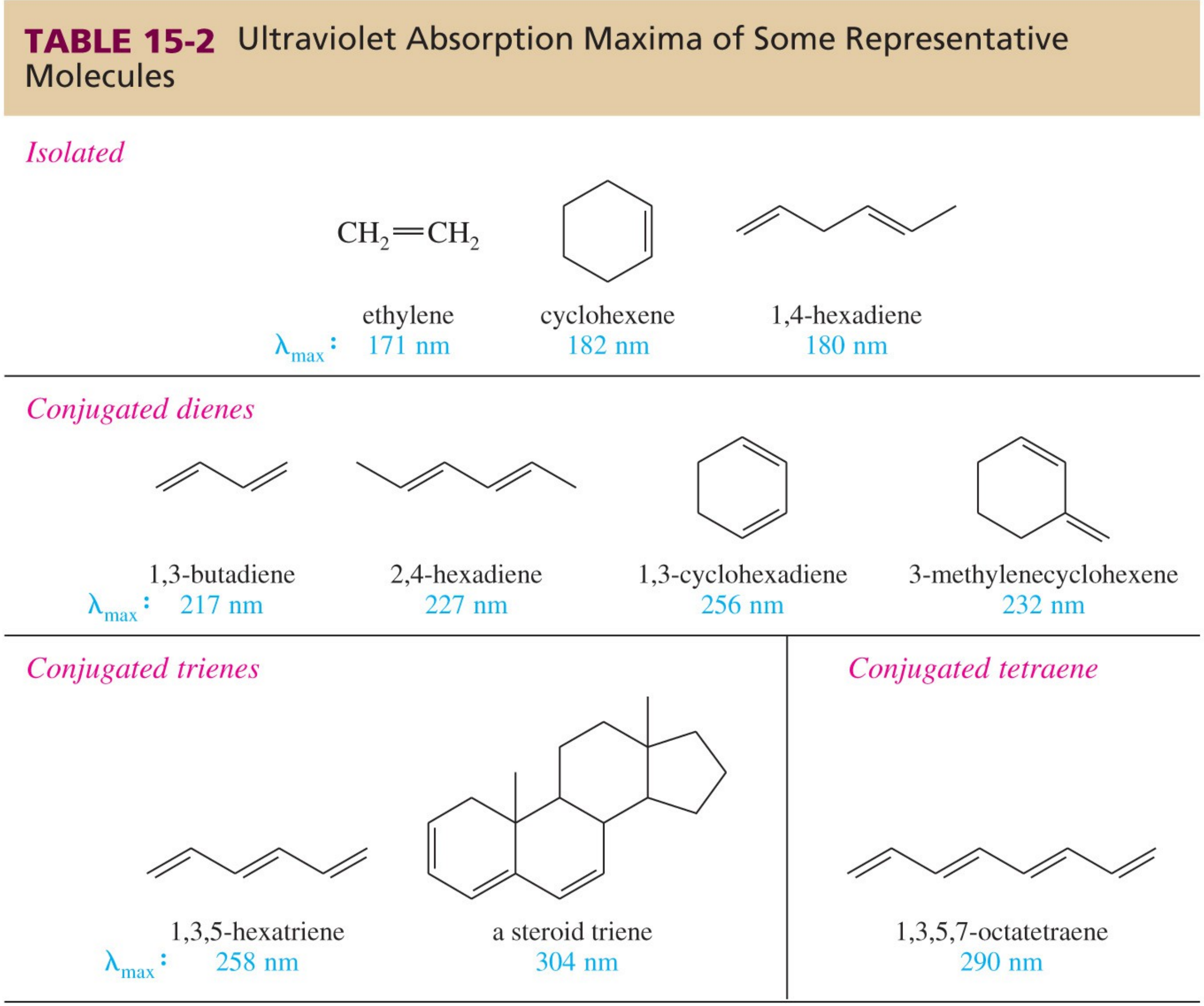


TABLE 15-2 Ultraviolet Absorption Maxima of Some Representative Molecules

Isolated

$CH_2{=}CH_2$

	ethylene	cyclohexene	1,4-hexadiene
λ_{max}:	171 nm	182 nm	180 nm

Conjugated dienes

	1,3-butadiene	2,4-hexadiene	1,3-cyclohexadiene	3-methylenecyclohexene
λ_{max}:	217 nm	227 nm	256 nm	232 nm

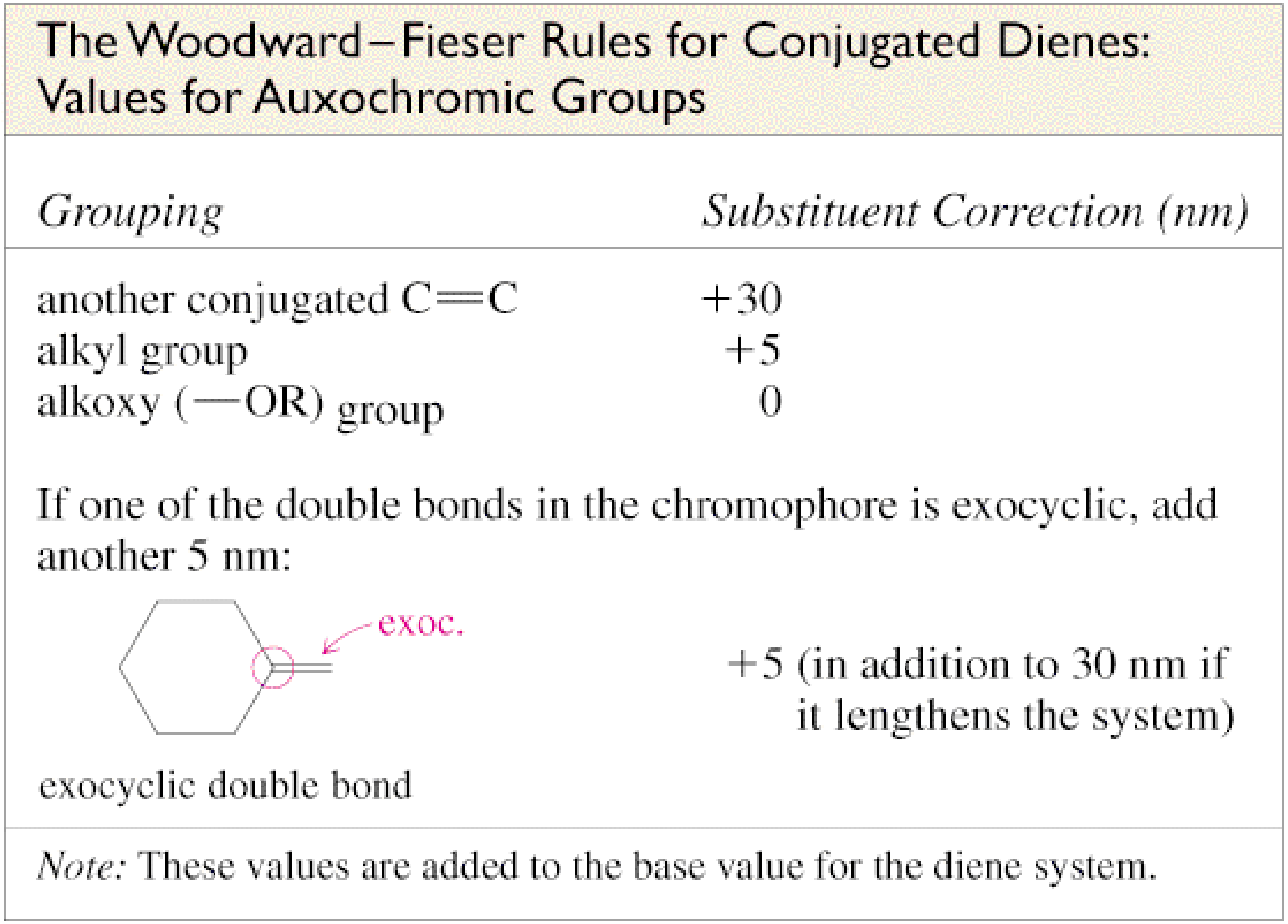
Conjugated trienes

	1,3,5-hexatriene	a steroid triene
λ_{max}:	258 nm	304 nm

Conjugated tetraene

1,3,5,7-octatetraene
290 nm

Woodward–Fieser Rules



The Woodward–Fieser Rules for Conjugated Dienes: Values for Auxochromic Groups

Grouping	*Substituent Correction (nm)*
another conjugated C═C	+30
alkyl group	+5
alkoxy (—OR) group	0

If one of the double bonds in the chromophore is exocyclic, add another 5 nm:

exoc.

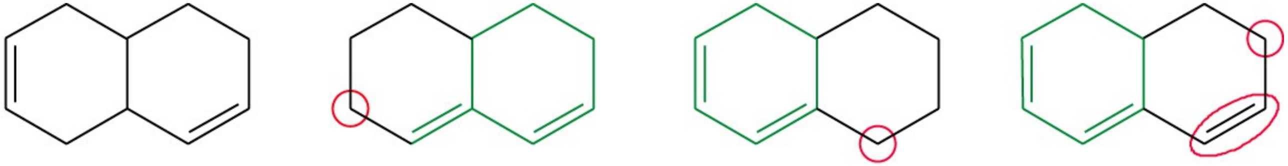
+5 (in addition to 30 nm if it lengthens the system)

exocyclic double bond

Note: These values are added to the base value for the diene system.

Solved Problem 2

Rank the following dienes in order of increasing values of $_{max}$. (Their actual absorption maxima are 185 nm, 235 nm, 273 nm, and 300 nm.)



Solution

These compounds are an isolated diene, two conjugated dienes, and a conjugated triene. The isolated diene will have the shortest value of $_{max}$ (185 nm), close to that of cyclohexene (182 nm).

The second compound looks like 3-methylenecyclohexene (232 nm) with an additional alkyl substituent (circled). Its absorption maximum should be around (232 + 5) nm, and 235 nm must be the correct value.

The third compound looks like 1,3-cyclohexadiene (256 nm), but with an additional alkyl substituent (circled) raising the value of $_{max}$ so 273 nm must be the correct value.

The fourth compound looks like 1,3-cyclohexadiene (256 nm), but with an additional conjugated double bond (circled) and another alkyl group (circled). We predict a value of $_{max}$ about 35 nm longer than for 1,3-cyclohexadiene, so 300 nm must be the correct value.